STUDY OF ACTIVATION OF COAL CHAR

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ABSTRACT

This is the final report on a project whose aim is to explore in a fundamental manner the factors that influence the development of porosity in coal chars during the process of activation. It is known that choices of starting coal, activating agent and conditions can strongly influence the nature of an activated carbon produced from a coal. This project has been concerned mainly with the process of physical activation, which in fact involves the gasification of a char produced from a coal by oxidizing gases. This is of interest for two reasons. One is that there is commercial interest in production of activated carbons from coal, and therefore, in the conditions that can best be used in producing these materials. Much is already known about this, but there is a great deal that is in the realm of “trade secret” or just “industry lore”. The second reason for interest in these processes is that they shed light on how porosity develops during any gasification process involving oxidizing gases. This has implications for understanding the kinetics and the role that “surface area” may play in determining kinetics.

In earlier reports from this project, several conclusions had been reached upon which the present results rest. There is an often-cited difference in use of nitrogen and carbon dioxide as molecular probes of carbon porosity when using vapor adsorption techniques. Carbon dioxide is often “preferred” since it is argued that it offers greater access to fine microporosity, due to the higher temperature of carbon dioxide as opposed to nitrogen measurements. The early phases of this work revealed that the extreme differences are observed only in chars which are not much activated, and that by a few weight percent burnoff, the difference was negligible, provided a consistent theoretical equation was used in calculating uptake or “surface area”.

In another phase of this study, it was noted in a preliminary way how the use of different oxidizing environments would lead to very different porosity development in the same char. There did not seem to be a link to the overall inherent reactivity of the gas-char combination to

the pattern of porosity development.

In another portion of this study, it was observed that the expected pattern of porosity development could be seen, as a function of whether the process was carried out in a pure chemical kinetic control regime (Zone I) or in a partially mass transfer control regime (Zone II). This portion of the study was useful in suggesting that the unburned carbon from many practical pulverized coal combustion processes had actually emerged from a Zone II environment. This confirms other published hypotheses, and strongly suggests that the material does not survive the boiler environment because it was produced in a purely oxygen mass transfer limited zone (so-called Zone III) or because it was simply so unreactive that it could not burn up in the allotted time (a pure Zone I argument). Moreover, it is believed that the very rapid initial opening of porosity that is revealed by the rapid disappearance of nitrogen and carbon dioxide accessible porosity may be associated with a very thin surface layer of pyrolytically-formed carbon that effectively blocks the bulk char structure from nitrogen. Once removed by low extent of burn-off this phenomenon disappears.

Finally, the project turned to comparing the relative influences of the starting coal and the oxidizing environment on the nature of porosity that was developed. Once again, the Argonne Premium coal suite served as a source of chars that would be representative of the broad range of coals found and utilized in the US. The conclusion is that the starting coal has a profound influence upon the ability of an oxidizing agent to develop porosity in the char. This is the single most important factor. Beyond this, however, there was a surprise to the extent that the ordering of porosity development did not follow a simply predictable pattern related to the reactivity of the activating agents. Oxygen is a very effective activating agent, if operation can be kept under control under so-called Zone I conditions. Its effectiveness is comparable to that of the more widely-employed steam.

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INTRODUCTION

This project is concerned with the factors that determine the development of porosity in chars derived from coals. The porosity is an essential characteristic of activated carbon products. Char porosity and surface area also play an important role in combustion (or gasification) of coals. For both reasons, it is some considerable interest to see how the porosity is affected by various factors associated with pyrolysis, combustion, or gasification.

The use of oxidizing gases in what are termed “physical activation” processes represents the simplest way to produce activated carbons from a coal feedstock. Naturally, the coal feedstock will have been subjected to a pyrolysis process as a first step, forming a char material that is actually the starting material for physical activation. This study has looked at some aspects of the preparation conditions- specifically, is the nature of porosity significantly affected by slow heating during pyrolysis, as compared with the extremely fast heating that particles suffer during pulverized coal combustion. To a significant degree, it has been observed that this vast difference in pyrolysis regimes has made very little difference to the porosity developed. What is far more important is the nature of the starting coal itself, as that seems to permanently imprint upon the char structure its propensity to form porosity. This is, incidentally, why chemical activation, involving reagents added to the char-forming material, do actually influence the pathways to char- these additive materials alter the actual chemical makeup of the starting material, and can drive the pyrolysis/activation process in new directions. Again, chemical activation is not of interest in the present study.

A second factor that has already been noted to play an important role in the nature of porosity development is mass transport during gasification (physical activation). The access that the oxidizing gas has to the interior of the particle plays a vital role in determining how well the inherent porosity of the char can be opened. The chemical kinetic control regime offers the only real hope of developing the full spectrum of available porosity. This is why use of oxygen in a combustion-type

process is of limited commercial interest. Practical char combustion processes can be at least partially pore-transport controlled, even in pulverized coal firing [1]. Much of the practical-scale pulverized combustion that takes place in utility boilers is almost completely mass transfer controlled, meaning that the oxidizing gas (oxygen in that case) reacts as soon as it finds the surface of a coal/char particle and has no opportunity to penetrate to the interior and open up porosity there. Again, the issue of mass transport in these situations has an importance apart from any interest in preparation of activated carbons. The proper design of combustion facilities demands that the kinetics of combustion be understood. Much combustion literature suggests that char reactivities should be expressed on a surface area basis [2], although small char micropores might not be fully utilized during oxidation or gasification [e.g., 3-8]. Many models have been proposed to describe development of char surface areas with burn-off [9-15], but many features need further clarification - e.g., different patterns of porosity development are observed in the same char, in different gases, even when rates of reaction are set to be identical [7, 16]. While this study cannot fully answer the question of the extent of internal microporosity utilization, some results clearly indicate that opening up of this porosity does impact observed kinetics in a chemical control regime.

The final phase of the program returns to two questions regarding the selection of activation conditions. It again examines the role of the reactant gas in determining the development of porosity. In this phase of the study, the full range of Argonne coals is studied in a systematic way. A significant addition to the experimental matrix is the addition of steam as a reactant. This is the activating agent of widest commercial use, and it is important to compare how it behaves with the behavior of the other oxidizing gases.

A second feature examined in this final phase of the work is the role of the mineral matter in the coal. The mineral matter is almost completely retained in the char during pyrolysis. It is well-established that this mineral matter can play a vital role in determining the kinetics of gasification in many circumstances. The question that is addressed here is whether the mineral matter will also impact the development of porosity in the chars.

EXECUTIVE SUMMARY

Coal is an important feedstock for the preparation of certain kinds of activated carbon products, and there continues to be significant interest in developing other high value added products from coals. One of the main difficulties associated with the development of products is the highly empirical nature of the process. Attempts to introduce a new feedstock or new activation condition require a great deal of experimental investigation, since no reliable predictive models of the porosity development process are available. There are two main characteristics that determine the properties of an activated carbon, once it is prepared- the nature of the porosity, and the chemical nature of the surfaces of the carbon. This project is mainly concerned with the first of these, as the ability to manipulate the second is available, once a suitable carbon structure has been prepared. The problem of porosity development during combustion, gasification, or activation is of considerable fundamental interest, beyond the general application area of main interest in this project.

Early phases of this project established that there is a basic porous structure imprinted upon a char when it is prepared from a coal, and that the ability to use physical activation is somewhat restricted by this imprinting. It was also shown that different reactant gases have differing abilities to open up the pore structure, and that mass transport aspects of the activation process also play a significant role in determining the course of pore structure development, within the bounds defined by the starting material itself.

The project involved a close examination of the effect of oxidizing gas on the activation of a range of different coal chars. In particular, during this phase of the project, attention turned to the use of oxygen, steam, carbon dioxide and nitric oxide as activation agents. Steam is a commercially preferred activation gas. In this examination, it does indeed provide among the highest extents of porosity development, but often surprisingly not much more than oxygen when the latter was used in a carefully controlled Zone I (kinetic control) reaction environment. By itself, use of steam cannot overcome the influence of the starting structure on porosity development- a softening coal remains a poor choice for high surface area development, (at least in physical activation).

The effects of native mineral matter, and its removal, were also explored in this study. It is seen that the removal of mineral matter has the expected consequence of lowering reactivity and generally influencing kinetic behavior. On the other hand, it is seen that the mineral matter is of limited importance when it comes to determining the porosity of the resultant char. Its influence is seen in the development of microporosity and small mesoporosity. It can significantly alter the pore size distribution obtained from a given char, but it cannot generally shift a char from being one prone to low porosity to high porosity development, or vice versa.

The results also clearly spoke to the lack of importance of certain variables relative to others. For example, orders of magnitude changes in heating rate had apparently little effect on the nature of porosity that was formed (the starting material was much more important). Also, the partial pressures of activating agents played little role in determining pressure. Of the reaction conditions employed with a given gas, the main determinant of how much porosity was opened was whether the reaction was allowed to slip from intrinsic rate control into partial diffusion rate control.

The final conclusion is that the choice of activating agent and conditions shows some effect on porosity development, but this is not nearly as significant as the influence of starting material structure. The presence or absence of mineral matter was not a particularly critical factor in determining the structure of porosity. What was perhaps surprising was the fact that different activating agents gave different trends with different carbons. This is reflecting a degree of sensitivity to the starting char chemical structure, which could not readily be predicted from the published literature. It was also clear that the choice of adsorptive gas used for examining the porosity can significantly affect the impression of porosity development during the processes. The use of carbon dioxide appears, as a general rule, to be problematic, as compared to the use of nitrogen, in spite of the well-known issues regarding activated diffusion barriers to the latter.

1.0 Experimental

1.1 Materials

Oxidation experiments were performed on chars derived from coals from the Argonne Premium Coal Sample Bank [17]. Chars were prepared in inert gas from the coal samples by one hour, 1273 K pyrolysis in a laboratory tube furnace (earlier results had shown little effect of temperature in the range 1173 to 1323 K). These chars should be typical of what might be termed “laboratory chars” which are often prepared by this sort of slow heating in a tube furnace.

1.2 Demineralization

For certain tests in this part of the program, char samples were demineralized following pyrolysis. There is often raised a question as to what effect demineralization has if performed before as opposed to following pyrolysis. This is not a question that is very easy to answer. Minerals can have an effect on pyrolysis as well as on the subsequent gasification. If present, they affect the pyrolysis, which means that they affect the basic structure of the char, which has already been shown to have a profound influence on the ability of the material to form porosity on subsequent gasification. So if the minerals were removed prior to pyrolysis, the effects of demineralization would be seen on two processes, and it would be hard to separate the effects of one step as opposed to the other. On the other hand, by demineralizing after pyrolysis, the effect of the minerals is restricted to effect on gasification alone. Here, it was accepted that both factors might contribute, but the effort was made to try to reduce all of the effects of the mineral matter by removing it from the raw coal.

The demineralization involved acid washing the raw coal prior to its pyrolysis. This involved placing roughly 5 grams of powdered sample into a 500 ml teflon beaker along with 10 ml of 5N hydrochloric acid and 10 ml of 5N hydrofluoric acid. The beaker was stirred with a teflon rod, so as to completely mix the sample and acid. Any solid adhering to the rod was washed off using deionized water, and the latter was removed. The beaker was covered with a teflon plate, and was

itself placed on a hot plate maintained at 60°C. After heating for two hours, the heat was turned off and the acid solution was evaporated off at near ambient conditions. Once the sample was dry to appearance, 25 ml of hydrochloric acid and 50 ml of deionized water were added back to the sample, and left to stand for about 10 minutes. The mixture was then filtered, and the remaining coal or char washed with deionized water until the wash water reached a pH of at least 6. This is a modification of other HF/HCl demineralization procedures employed elsewhere, and has the clear disadvantage that the mineral-laden HF/HCL solution is not directly decanted. This is a choice made to minimize physical handling of this dangerous mixture. Once the HF is removed, the HCL will redissolve most of the extracted minerals, and that solution is much safer to handle in the decanting processes.

The efficacy of the demineralization varied with the coal. In the case of Wyodak char produced from demineralized coal, the final ash content was about 2% by mass, as compared with the usual 20%. The procedure was not as successful for Illinois No. 6 coal, as it removed about 55% of the mineral matter. It should be noted that even when more severe demineralization is employed, it is virtually never the case that the resulting char is entirely free from all inorganic components- it is always a matter of degree of removal. Since even trace amounts of inorganic matter can exert some influence on kinetics, the best that could be expected from the present experiments is an indication of the extent to which minerals might influence the process. Hence in the present study, the search was aimed at uncovering any major differences, as opposed to quantifying subtle differences.

The composition of the main ash components was also determined. The table below shows the ash compositions determined by atomic absorption techniques for the raw and partially demineralized samples. The results clearly caution against calling the acid-washed samples “demineralized”, since there are still all of the original minerals contained in the ash of the acid-washed samples. The minerals may have changed in composition or physical state of aggregation during the treatment- this was not determined. All that was here determined was that the removal of

the mineral did not significantly impact the nature of the starting char, in terms of its porosity.

Ash Compositions of Raw and Acid-Washed Coals

<u>Element %</u>	<u>Raw Ill. No. 6</u>	<u>Treated Ill. No. 6</u>	<u>Raw Wyodak</u>	<u>Treated Wyodak</u>
Al	7.33	0.61	8.35	5.15
Ba	0.04	0.04	0.40	0.25
Ca	4.74	3.21	15.44	9.32
Fe	14.05	15.60	4.12	2.72
K	1.02	0.11	0.24	0.16
Mg	0.39	0.06	2.77	1.77
Mn	0.05	0.03	0.03	0.02
Na	0.51	0.01	0.98	0.58
P	0.01	0.0	0.35	0.21
Si	16.37	0.95	13.22	8.43
Sr	0.01	0.01	0.42	0.26
Ti	0.40	0.29	0.65	0.43

1.3 Sample Gasification and Reactivity Testing

Chars were gasified in a thermogravimetric system in air. Samples of 10-50 mg of char or fly ash were dispersed on circular platinum pans, resulting in particle beds of ≤ 1 mm thickness. Temperatures were generally selected to assure that gasification took place under reaction rate-controlled (so-called "Zone I") conditions, but in certain cases, pore diffusion-limited burning was also studied (so-called "Zone II" conditions).

1.4 Porosity Characterization

The most common method for characterizing the porosity of chars is gas adsorption. This test is relevant, insofar as it models the processes in use of activated carbons in gas adsorption as well as the processes in combustion or gasification. In either case, small gas phase species must penetrate the carbon substrate, in order for the porosity to be "useful".

Adsorption isotherms were determined for chars using an automated volumetric gas adsorption apparatus (Autosorb 1, Quantachrome Corp.). Adsorption of N₂ and CO₂ were performed at 77 K and 195 K, respectively. Nitrogen was the preferred adsorbate for reasons

discussed previously [7,18, 19].

2.0 Results and Discussion

2.1 General Aspects of Activation in Oxygen

This section of the report presents a group of typical results for activation of Illinois No. 6 char in air, as a lead-in to the more detailed discussions that follow on various topics. Figure 1 shows kinetic data obtained for burning illinois No. 6 chars in air. The results are expressed as the mass loss rate per remaining mass, $dm/dt \cdot (1/m)$. The figure shows results that speak to the influence of two important variables that influence the course of porosity development- burnoff and mineral content.

The solid points of Figure 1 are for samples that contained the full amount of mineral from the raw coal, while the open points are those that came from the partially demineralized coal. It is immediately apparent that there is an influence of demineralization, even if the demineralization of the coal was incomplete. On the other hand, comparison of the two sets of intersecting solid lines strongly suggests that there was no fundamental change in gasification mechanism as a result of demineralization. It merely looks as though the reactivity of the solid dropped uniformly in all temperature ranges. This has been interpreted elsewhere as reflecting a loss of reactive sites in the sample. This issue will not be pursued further here.

Figure 1. The gasification kinetics of Illinois No. 6 char in air. Solid points, samples from raw coal; open points, samples from demineralized coal. The dashed lines show results from experiments in which the char was used without any initial burnoff.

Many factors can influence the reactivity of a coal char, including composition/rank [e.g., 20, 21] maceral composition [e.g., 22], heating rate [e.g., 23], thermal annealing [e.g., 24] and the presence of catalytic matter [e.g., 25-28]. It has been reported that catalytic impurities can lead to greater meso- and macro-pore and less micro-pore formation [29-32]. The influence of catalytic matter on the porosity will be examined further below.

A second feature is visible in Figure 1 that has been noted in other previous parts of this study. There is clear evidence from a Zone I to Zone II transition as temperatures of gasification are increased. In the case of the demineralized samples, the transition (seen as the break between the

two solid line sections) occurs at around 750 K, while in the more reactive higher mineral sample, the break takes place at around 740 K. Above these temperatures (i.e., at lower values of $1000/T$), the Arrhenius activation energies appear to be near 100 kJ/mol, whereas below these transition temperatures, the activation energies are near 200 kJ/mol. This result is in accord with the predictions of an onset of internal mass transport limitations and a transition from Zone I to Zone II conditions in the temperature range from 740 to 750 K. It is very important to keep in mind the effects that mass transport limitations can have on the development of porosity. In this study, unless otherwise explicitly noted, the burnoffs were accomplished under Zone I conditions, which generally give the highest development of surface area.

Finally, Figure 1 illustrates well a problem that is often encountered by researchers whose primary interest is in the kinetics of gasification. Quite apart from the question of whether mass transport influences results in the manner discussed above is a question of how surface accessibility influences the observed kinetics. The points shown as joined by dashed lines were obtained in experiments in which the char was not burned off before low temperature reactivity experiments were begun. These points should be compared with those obtained on sample that had been burned off to 20% mass loss prior to the experiments shown here. It is immediately apparent that the points from the 0% burnoff experiments show lower rates than those obtained from the experiments in which 20% burnoff was done in preparing the samples. These experiments were deliberately conducted in the direction of low temperature to high temperature to bring out more clearly the consequence of development of surface area with burnoff. Both the increase in temperature and increase in accessible surface area contribute to the apparent increase in reactivity of the 0% burnoff samples. Once a certain point of a few percent burnoff is passed, the influence of opening up of surface area becomes relatively small and the fact that a sample was or was not burned off prior to experiments becomes irrelevant. In this work, 20% was generally chosen as an initial treatment. Figure 2 shows that even though a significant development of porosity takes place with just a few percent burnoff, a higher degree of burnoff is required to get to a condition in which the degree of

burnoff does not matter.

Had the experiments of Figure 1 with 0% burnoff samples not been done with a steady increase in temperature, and the temperature had instead been jumped between high and low values, there is a good chance that a few points might have just appeared to be subject to a higher degree of “scatter” from the true Zone I curve that emerges from experiments at above 20% burnoff. Between this artifact and the actual Zone I to Zone II transition, it is little wonder that the literature contains a great many studies exhibiting considerable scatter in what are presented as nominally “intrinsic” kinetic data. This is an example of the care that needs to be exercised in examining data on the kinetics of char gasification.

Figure 2. The influence of extent of prior burnoff on measured kinetics of air gasification of Illinois No. 6 char. Burnoff values prior to these experiments are as indicated.

A question might be posed as to why, in Figure 1, the transition from Zone I to Zone II does not occur at the same value of intrinsic reactivity in both mineral-containing and demineralized chars. The answer appears to be found in the fact that the nature of reactivity does depend upon what was done with the minerals, through an effect on porosity. This issue will be taken up later in this report.

Figure 3 shows the course of experiments used in preparing the chars for porosity testing.

Figure 3. Typical burnoff experiments, involving Illinois No. 6 char in air. In one case, the heating was stopped at 5% burnoff, in another at 20% and in a third the sample was allowed to fully combust. In all three cases, the isothermal combustion period involved a temperature of 448°C.

Figure 3 shows the course of three typical burnoff experiments. There is initially a low temperature period, at about 120°C, designed to allow any moisture to evaporate. It is apparent that the moisture content of these samples is very low (less than a percent by mass). Then the samples are rapidly heated to 448°C (in this example) and allowed to isothermally react at that temperature to the desired degree of mass loss (in this example, 5%, 20% or complete combustion to ash). It is apparent from the figure that there is a high degree of reproducibility in the temperature traces as well as in the mass loss traces. It is the products of these sorts of preparation experiments that have

been examined with regard to porosity development.

Figure 4 shows typical initial porosity characterization data, obtained by the nitrogen adsorption method that was applied for virtually all samples in this phase of the study. It needs to be recalled that in earlier phases of this project, it had once again been demonstrated that nitrogen was a superior adsorbate to carbon dioxide when it came to characterization of these materials. This is because while nitrogen is limited in its ability to access micropores only at near zero burnoff, carbon dioxide is unable to as fully interrogate larger porosity in the samples. Micropores are defined as pores of widths or diameters less than 2 nm, and mesopores are those with diameters or widths larger than this, but smaller than 50 nm.

Figure 4 shows isotherms at various levels of burnoff. The zero burnoff isotherm for this char is essentially coincident with the p/p_0 axis, and is not explicitly shown. Several important features are immediately visible from this plot. One is that the total porosity increases progressively with burnoff, i.e., that the sample is indeed activated. This is especially apparent in the data obtained under Zone I conditions. The values of nitrogen uptake very near a p/p_0 of zero are indicative of microporosity. It is seen in the Zone I results that microporosity increases continually with increasing burnoff, at least to the limit of these experiments (66% carbon burnoff).

The degree to which the adsorption isotherm data show an increase in slope in the midrange of p/p_0 values qualitatively indicates an increase in mesoporosity. It is apparent that with an increase in burnoff under Zone I conditions, there is also a considerable increase in mesoporosity.

There is some debate in the literature about whether the rapid development of microporosity is a result of “drilling” of new pores in the carbon, or merely the uncovering of existing “free volume” within the disordered carbon. The common belief is that the development of mesoporosity involves widening of micropores, or the removal of walls between adjacent micropores. These theories will be further examined below.

Figure 4. Nitrogen adsorption/desorption isotherms obtained on Illinois No. 6 chars gasified in air under Zone I (open points) and Zone II (closed points) conditions. Zone I involved a temperature of 728 K, whereas Zone II experiments were performed at 758 K.

The opening of a hysteresis loop in the adsorption/desorption isotherm at a p/p_o above 0.4 is a common observation, and it is attributed to the difference in mechanisms of filling micropores and larger pores. Again, this phenomenon becomes more important, the greater the development of larger porosity.

Under Zone II conditions, microporosity development occurs to a more limited extent than under Zone I conditions. This is immediately apparent by comparison of the isotherms at similar

percentage burnoffs, under Zone I and Zone II conditions. This observation would be consistent with a model of diffusional limitation at a larger pore size (larger than micropores). These larger pores serve to feed the interior of the particle, where the potential micropore volume already exists but has not yet been opened. For any given degree of burnoff, under Zone II conditions, more carbon mass is eaten away from an accessible exterior shell, and this mass loss is not associated with opening micropores within the interior. Figure 5 shows results from another series of experiments on the same char, in which the isotherms of two samples of virtually identical burnoff (of 51 to 52%) samples are plotted. By matching the two curves in the micropore region (through an upward shift of the Zone II curve), it is clear that the development of mesopores is also slightly greater in the Zone I case. It should also be noted that the samples in this series were not identical with the samples shown in Figure 4 (they were from another batch) so the isotherms in these two figures cannot necessarily be compared.

The trends in the data of Figure 4 defy simple explanations. It may be quickly seen that only when the burnoff exceeds 10% does the development of porosity with burnoff depend upon burnoff level, and therefore the distinction between Zone I and Zone II also depends upon this variable. Then, there appears to be a period at higher burnoffs during which the extent of microporosity development under Zone II conditions is obviously less than that under Zone I conditions. It is not clear why this should be the case only at burnoffs greater than 10%, and this warns about the ability to offer “simple” explanations of the porosity behavior based purely upon the kinetic regime. The behavior in the mesopore region, at high burnoffs (Figure 5) appears consistent with what would be expected from Zone I vs. Zone II behavior. The more able the reactant is to penetrate the pores, the more porosity that can be opened up.

Figure 5. Two samples of Illinois No. 6 char burned off to approximately 51%. Closed points are actual data for a sample prepared under Zone I conditions. Open points are for a sample prepared under Zone II conditions, shifted upwards by 47 cc/g-carbon.

Figure 6 shows the typical sort of calculated result that can be obtained from the isotherm data of Figure 4. The calculations of BET area (and in later sections of this report, micropore volume, from Dubinin-Radushkevich (DR) theory) followed the standard methods [33]. Figure 6 makes clear that the surface area, which depends most heavily upon the micropore content of the sample, increases to a much greater extent under Zone I conditions than under Zone II conditions. This is consistent with what could have be inferred from the isotherms of Figure 4 themselves, but calculated and displayed in a different way. It might be noted in passing that the ability of the

Illinois No. 6 char to develop high surface areas, as shown, is not the general case for softening bituminous coals, and might have to do with the relatively facile crosslinking that this coal undergoes during pyrolysis, as compared with other bituminous coals.

Figure 6. Increase in nitrogen BET surface area during air activation of Illinois No. 6 coal char under Zone I and Zone II conditions.

Figure 7 shows the data of Figure 4 analyzed for small pore size distributions using density functional theory (DFT) [34,35]. The calculations were performed using an integration kernel for nitrogen on carbon provided by Quantachrome Corporation. Once again, this method of analysis does not provide a different conclusion than could be drawn from the raw data of Figure 4, but it offers another quantitative insight into the real size distributions.

Figure 7. Cumulative pore size distributions in Illinois No. 6 coal chars gasified in air to the indicated burnoffs, under pure intrinsic rate control (Zone I) or under internal diffusion control (Zone II). Same data as in Figure 4, analyzed using DFT theory (see text).

Once again, the similarity of porosity development under Zone I and Zone II conditions is seen at burnoffs lower than 10%. In this representation of the data, the picture becomes more clear that it is pores in the larger micropore and smaller mesopore, ranges that become the locus of difference between Zone I and Zone II conditions. To the extent that mesopores do not exist as “free volume” in the original solid, as is the case with the micropores that are uncovered at low burnoff levels, then pores in the mesopore range must be accessed during burnoff, so as to enable their growth.

It is just within the length scale from 25-30 Å that Shim et al. [36] noted the ordering parameter of pyrolytically prepared Illinois No. 6 coal char to precipitously decline. This order parameter is an indication of the size of ordered crystallites within the char. Hence the main growth in porosity is seen to take place on a scale that is larger than the crystallite size. This would indicate a process in which pieces of the structure, at least comparable in size to these crystallites, must be removed to create new porosity.

This report will now turn to the influence of different experimental variables on the development of porosity. Earlier reports in this project have detailed the comparative behavior of the Argonne coal-derived chars in air.

2.2 Surface Area Development in Laboratory Chars Under Zone I Conditions

The patterns of surface area development in laboratory-prepared chars were explored using the same techniques as above. Oxygen partial pressure variations from 1 to 21 kPa did not influence these results, consistent with results from another type of char [36].

Figure 8 shows surface area development in the full set of Argonne coal-derived chars. These results were already reported in another project report, but are repeated here for ease of reference. All surface areas increase with burn-off, at least initially. The ultimate extent of surface area development in the medium- and higher rank high- volatile bituminous coals (Pittsburgh No. 8, Lewiston-Stockton and Upper Freeport) is in the same range as for utility chars. The low volatile bituminous coal (Pocahontas) reaches somewhat lower surface areas than do the preceding lower rank coal chars. On the other hand, the lowest rank bituminous coals (Blind Canyon and Illinois No. 6) reach much higher surface areas.

All of the coal chars exhibit a steep increase in surface area with burn-off, near zero burn-off (the fresh char state). This behavior is well-known [e.g., 7], and as noted above is partly attributable to an artifact of the measurements, having to do with nitrogen diffusional limitations at 77K [7, 18]. To re-emphasize another point, the use of the BET equation for microporous solids is

questionable, but common, practice due to its convenience and the ease of comparison afforded by a simple numerical value [18, 33].

Figure 8 shows three different classes of behavior. There is the behavior of the non-softening lignite and subbituminous coal (Beulah and Wyodak) which involves the rapid opening up of free volume which is presumably present from the time that the chars undergo the crosslinking in the pyrolytic process. This is why with very limited amounts of burnoff, such large amounts of microporosity are revealed (and probably not created). On the other end of the spectrum are the highly caking bituminous coals, (including the Pittsburgh No. 8, the Upper Freeport, the Lewiston-Stockton and the Pocahontas. These coals form a very ordered structure upon pyrolysis and cannot develop a high degree of microporosity regardless of degree of burnoff. Finally, in between the two extremes are the geologically younger bituminous coals- the Illinois No. 6 and the Blind Canyon. These can develop high microporosity, much as do the non-softening coals. They do so because they more readily crosslink in a disordered structure during pyrolysis, because both of these bituminous coals have a high oxygen functional group content. On the other hand, the development of microporosity does await a significant degree of burnoff, and is therefore not available immediately as it is in the non-softening coals.

Figure 9 shows the development of porosity in the same suite of coals, using CO_2 as the activating agent. All of the results in Figure 9 were obtained under Zone I conditions. The temperatures involved in these activations were considerably higher, because the reactivity of carbons in CO_2 is much lower than in O_2 for any temperature of practical interest.

Just as for the results of gasification of the chars in oxygen, the results for gasification in carbon dioxide show two extremes of behavior. In the case of the Wyodak and Beulah samples, once again the surface area starts out high and rises to even higher values with increased gasification. These samples behave as though they have an inherently high microporosity from the outset, that is simply revealed by small amounts of gasification. At the other end of the spectrum of behavior are again the softening bituminous coals- the Pittsburgh No. 8, the Upper Freeport, the

Figure 8. Development of surface area during combustion in air of laboratory coal chars. The temperature of combustion is indicated.

Pocahontas and the Lewiston-Stockton. Exhibiting intermediate behavior are the Illinois No. 6 and Blind Canyon samples. The actual reactivities of the samples on a per unit of carbon mass basis vary by approximately an order of magnitude, consistent with a variation in surface area of samples of about the same range. What this means is that the main determining factor for observed differences in carbon dioxide reactivity is the surface area of the samples (this will be explored further below).

Generally speaking, the results for activation in CO_2 give pore surface areas that are comparable to, but a bit lower than those developed in oxygen. The inescapable conclusion from these results is that it is the starting material itself that is the primary determining factor in development of surface area and fine porosity. There is a fundamental material structure that limits

the amount of fine porosity that can be developed. This porosity development is insensitive to the temperature at which the activation is performed, as the activation in CO₂ may be seen to require much higher temperatures than did

Figure 9. Development of surface area during carbon dioxide gasification of laboratory coal chars. All of these samples were examined under Zone I conditions. The temperature of the activation experiments is indicated in the legend.

activation in oxygen (air). Figure 10 illustrates the comparison of air and carbon dioxide reactivity for one of the chars examined- the Illinois No. 6 char. It may be clearly seen how vastly different the kinetics are for the two reactants, and the same is true for all of the other chars as well. The selection of Zone I activation conditions was guided by a knowledge of the kinetic data of these kind, as already explained above. Figure 10 shows the narrow band of reactivity that was used for

preparing the different burnoff samples that were examined for porosity. The choice of conditions was naturally dictated by the practical need to achieve a desired degree of burnoff in a reasonable time.

Figure 10. Kinetic rates for Illinois No. 6 chars in air and carbon dioxide (1 atm), showing the range of rates selected for Zone I char activation experiments.

Figure 11 shows the results of activation in steam (or more precisely, 55% water vapor, balance helium, at atmospheric pressure). The figure shows the same general trend as had been noted in the other activating agents, namely, that Blind Canyon develops significantly greater porosity than did Pittsburgh No. 8 or Upper Freeport coals.

A comparison of all three of these coal chars is shown in Figure 12, which summarizes the data for the three coals that were activated in all three media. It is quite apparent that while all three oxidizing gases gave comparable surface areas in all three gases, the steam and air gave consistently

higher surface areas than did the carbon dioxide activation.

Figure 11. Development of surface area during steam gasification of laboratory coal chars. All of these samples were examined under Zone I conditions. The temperatures of the activation experiments are shown in the legend.

Hence, the results in all three common oxidizing gases provide a consistent conclusion regarding the primary importance of the starting material in determining the ability to develop surface area. This has, of course, been recognized for some time in the activated carbon industry. It is precisely the agricultural byproducts whose behavior is most similar to that of low rank coals, that provide the highest surface area carbons.

In a different part of the study, the activation of carbons was examined in NO. It is not believed that NO will be a practical activating agent, but it is intriguing, insofar as its rate of reaction with carbons is somewhere between that of oxygen and carbon and that of steam or CO₂ and

carbon.

Figure 12. A comparison of the activation behavior of three coal chars in oxygen, steam and carbon dioxide. Data are from Figs. 8, 9 and 11.

Figure 13 shows a comparison of surface areas developed in oxygen and NO for the Wyodak subbituminous coal char and the Pittsburgh No. 8 coal char. It should be noted that this figure combines results from two different series of runs, with chars prepared from the same coal, but under slightly differing conditions (this is the distinction between A and B samples). For samples prepared from a single batch of char, it appears that in the case of Wyodak char, the porosity development is very similar in NO and in oxygen. The similarity in behavior does not extend to the samples prepared from Pittsburgh No. 8 coal.

In a separate part of this study, the behavior of a wide range of carbons was compared in

Figure 13. A comparison of BET surface area development in oxygen and in nitric oxide. The designations A and B indicate which batch of sample the particular char came from. Pittsburgh No. 8 char from batch B was gasified in 0.8 kPa of NO at 1023 K or in 2 kPa of oxygen at 773 K. As noted above, Pittsburgh No. 8 sample A was gasified in air at 732 K.

NO and in oxygen. The results are shown in Figure 14. These results show no clear trend regarding activating agent and BET surface area development- at times oxygen gives higher area, and at times it is nitric oxide. Hence, we do not have the ability to say with certainty which agent will lead to higher surface areas, even if we can say with certainty that the ability to develop surface area is somewhat similar in both gases, and clearly most determined by the nature of the starting material.

Returning for a moment to Figure 13, the fact that the Wyodak results with sample B are so similar in oxygen and NO speaks to the fact that the difference in oxygen between samples A and B

reflects a variability attributable to either the burnoff conditions or the sample preparation conditions. Since the chars in both A and B were prepared under nominally very similar conditions, the most logical explanation has to do with an effect of oxygen pressure and gasification temperature on pore development. The effects of concentration and temperature will be further discussed below.

Figure 14. The comparative behavior of different types of chars activated in NO and in oxygen, at the indicated temperatures.

In conclusion of this brief introductory section, it must again be emphasized that the most important variable in determining porosity development behavior is the composition of the starting material. There appears to be no combination of conditions that can be used to develop high surface areas in materials that soften and form a reasonably highly ordered char structure. It is the disorder

created by crosslinking of a carbon skeletal structure that produces the free volume that can become microporosity.

The next sections of this report will expand upon the above conclusions and explore how other variables can affect them. Also, there will be a consideration of porosity using other measures of its extent, which will provide a picture that is not as dominated by the influence of microporosity.

2.3 The Influence of Mass Transport Limitations

The consequences of operating under mass transport controlled conditions were already introduced in Figures 4 through 7, for the gasification of Illinois No. 6 coal char in air. In this subsection, the effects of mass transport limitations will be more fully examined for different chars and reactant gases. The conclusions drawn from the Illinois No. 6 results was that microporosity could not be developed as fully under Zone II conditions, when reactant gas diffusion into the interior of the particle was limited (visible from Figures 4, 6 and 7). Figure 5 suggested that mesopores also did not develop to as great an extent under Zone II conditions, and Figure 7 showed that it is the larger micropore, smaller mesopore range that was most affected by transport limitations during air gasification of the Illinois No. 6 char.

Figure 15 compares the development of porosity in a Wyodak coal char in NO under Zone I and Zone II conditions. Again, the results are displayed as BET surface area results which tends to emphasize the role of micropores. As in the case of the Illinois No. 6 coal char, activation under Zone II conditions clearly allows less development of surface area and microporosity.

Figure 16 confirms the trends that are implied in Figure 15. The development of microporosity takes place at a much lower burnoff in the Zone I samples than in the Zone II samples, as shown by the differences in the isotherms near P/P_0 of zero. Also, the greater slope of the isotherms obtained on Zone I samples, together with the opening up of the high P/P_0 hysteresis loop at lower burnoffs, indicates that Zone I samples develop a higher amount of mesoporosity than do Zone II samples. It should be noted that in drawing Figure 16, the adsorption volumes are

expressed on a gram of char basis, which is why the whole isotherm appears to shift downward at high burnoffs under Zone I conditions. The carbon in the sample at 67.9% burnoff is actually considerably more porous than is the carbon in the sample at 18.3% burnoff, but the ash fraction is essentially non-porous. .

Figure 15. Gasification of Wyodak coal char in 0.82 kPa NO at 911 K (Zone I) and 1027 K (Zone II).

Figure 17 shows the results of a Barrett-Joyner-Halenda (BJH) analysis [38] of isotherms from the same series of experiments depicted in Figures 15 and 16. This analysis focuses on the mesopore region of the isotherm (and is plotted as a differential pore volume, $dV/d[\log D]$). The results in Figure 17 compare the development of mesoporosity under Zone I conditions with that under Zone II conditions. It is very clear from these results that under Zone II conditions, there is never as much development of mesoporosity as there is under Zone I conditions, which again could have been anticipated from the isotherms themselves. When there is some mesopore development

under Zone II conditions, it comes at a preferred pore size that is the same as observed under Zone I conditions. This is also of little surprise, since it is not expected that the inability of the reactant to

Figure 16. Nitrogen isotherms for gasification of Wyodak in NO under Zone I and Zone II conditions. The data are those from which Figure 15 was prepared. The burnoffs are indicated as percentage of available carbon burned off.

access the interior of the particle would be of any particular importance regarding the mechanism, and thus size range, of pore formation. The peak in the apparent diameter of mesopores formed is at around 30 Å. These results also speak to the fact that once a particular extent of mesopore formation is achieved under Zone I conditions, then there is little more development of mesopores beyond that point. The increases in porosity come in the micropores and in the macropores. Again, this could have been anticipated from the shape of the isotherms. It is also very apparent how at high extents of burnoff, the formation of larger (macro-) pores is favored.

The results above indicate how complex porosity behavior is, with several different processes superimposed one atop another, with different processes dominating at different extents of burnoff. Figure 18 emphasizes, through a comparison of the mesopore size distributions obtained in three different oxidizing gases, how once again there is an apparent imprinting of the

Figure 17. BJH mesopore size distribution analysis of Wyodak coal char gasified in NO. The open points indicate sample prepared under Zone I conditions, and the closed points indicate samples prepared under Zone II conditions. Burnoffs are as indicated on the plot.

material with a certain pore size formation tendency, even in the mesopore size range. In this case, this imprinting will be shown below to be a consequence of the presence of certain catalytic agents within the char.

Figure 18. The BJH analysis applied to Wyodak chars gasified to the indicated extents in three different oxidizing gases. All results were obtained under Zone I conditions.

For comparison with the above behavior of Wyodak coal char, the results for Illinois No. 6 coal char, activated in a different medium, are shown in Figure 19.

These results again show a propensity, though much less clear than in the case of the Wyodak sample, to form pores in a certain mesopore size range. Once again, there is the hint of a preferred mesopore size range at around 20 Å, though it is not nearly as distinct as in the case of the Wyodak char. Also, consistent with the trends reported earlier, it is clear that Zone II gasification cannot open porosity on the mesopore scale nearly as effectively as can Zone I activation.

Figure 19. BJH analysis of porosity development in Illinois No. 6 coal char, gasified in air under Zone I and Zone II conditions.

Another example of the difference in pore development under Zone I and Zone II conditions is provided in Figure 20, which shows the comparison of pore development in Pittsburgh No. 8 coal char gasified with oxygen.

Figure 20. DFT analysis of porosity developed in Pittsburgh No. 8 coal char gasified with oxygen under Zone I and Zone II conditions. Burnoffs are indicated on the figure. The Zone I results were obtained at 743 K in air, whereas the Zone II results were obtained at 773 K in 2% oxygen.

There might be some concern regarding the effect of the oxygen pressure difference between the Zone I and Zone II experiments in Figure 20. It is not believed that this effect if present, is significant. Note that the trend precisely mirrors what was seen in Figure 4, in the results for another char derived from a softening bituminous coal (that from the Illinois No. 6).

Figure 21 shows the same results as used in Figure 20 interpreted using BJH theory.

Figure 21. Mesopore development during gasification of Pittsburgh No. 8 coal char under Zone I and Zone II conditions. The burnoff refers to carbon burnoff.

Consistent with the picture from Figure 20, the results of Figure 21 show that the gasification under Zone I conditions is more effective in opening a broad spectrum of pores ranging from those in the micropore region (to which BJH theory does not strictly apply) to those in the mesopore region.

Yet more examples of the differences observed in porosity development under Zone I and Zone II conditions are provided by the data for char derived from Beulah-Zap lignite, and presented in Figure 22.

Figure 22. Results of BJH analysis of nitrogen adsorption isotherms obtained on Beulah Zap lignite char, gasified in 1% oxygen. The Zone I points were taken at 703 K, while the Zone II points were taken at 803 K.

The results in Figure 22 show that as gasification proceeds under Zone I conditions, there is development of mesoporosity with an apparent diameter of 25 Å. When high burnoffs are achieved (i.e. 64% on a char basis, or taking into account the 16% ash content, 76% carbon burnoff), there is apparently a shift from microporosity towards large mesoporosity and macroporosity. Under Zone II conditions, while the preferred mesoporosity development occurs close to the same size range, the basic character of the char is retained to much higher burnoffs, as the char in the interior of the particle cannot be reached in order that it react to a significant degree.

One difference is notable between the results for the bituminous coal chars (from Illinois

No. 6 and Pittsburgh No. 8) as compared with the results from low-rank non softening chars (such as those for the Wyodak subbituminous and Beulah lignite). The BJH plots for softening coal chars (Figures 19 and 21) seem to exhibit a tendency to show a monotonically decreasing distribution of pore sizes from those in the micropore range into the mesopore range, while the BJH plots for the lower rank coal chars (Figures 17, 18 and 22) show a tendency towards forming a distribution with a distinct peak in the mesopore range. The influence of catalytic minerals will be explored below, in relation to this difference, and the theme of behavior in relation to Zone I vs. Zone II gasification will be revisited at that time.

Hence, it is clear from these very different examples that there is a major difference in development of porosity under Zone I and Zone II conditions. Where the Zone II conditions are explored, neither microporosity nor smaller mesoporosity can be as readily developed. This appears to be the case, regardless of whether the chars had undergone softening during pyrolysis. The nature of the porosity that develops in softening coal chars is somewhat different than the porosity that develops in non-softening chars, but generally speaking, the trends in porosity development are similar.

2.4 The Influence of Catalytic Mineral Matter on the Development of Porosity

Figure 1 has already illustrated the significant influence that catalytic mineral matter exerts on the kinetics of gasification of Illinois No. 6 char. The rate is observed to significantly decline upon the acid washout of some of the mineral matter. Catalytic impurities has been reported to lead to greater meso- and macro-pore and less micro-pore formation [29-32]. This part of the study will examine whether that is the case for both a high and low rank coal.

The influence of acid washing on the initial porosity of the Illinois No. 6 char is not great; until some gasification of the structure takes place, the adsorption volumes are so small as to be difficult to reliably measure. Hence, there is not a large difference in the initial pore structure of the

untreated and acid washed chars that can be used to explain the shift observed in Figure 1. Rather, it is that the kinetics of the gasification reaction that are modified by the demineralization of the coal prior to pyrolysis. The catalytic effect of the minerals that were removed is apparent,

Figure 23 shows the difference in observed surface area development in air, for the demineralized Illinois No.6 char and the untreated Illinois No. 6 char.

Figure 23. Nitrogen BET surface area of Illinois No. 6 chars gasified in air under Zone I conditions. The gasification of the demineralized sample took place at 734 K, whereas the gasification of the untreated sample took place at 728 K.

The results in Figure 23 show that the development of microporosity is initially quite similar in both cases. Only as higher burnoffs are achieved does the mineral-containing char show a greater degree of pore formation than does the demineralized char. The BJH pore size distributions obtained with demineralized and untreated chars are compared in Figure 24. Consistent with the above results on surface area, the results of Figure 24 again show that there is similarity of the porosity in chars produced at low burnoffs. There appears to be a greater degree of larger

micropore and smaller mesopore production in the untreated chars than in the demineralized chars.

Figure 25 shows the results of the DFT analysis of the same isotherms as used for Figures 22 and 23. Once again, the similarity of the porosity in the micropore range is quite apparent. There is little effect of the removal of a significant fraction of the mineral matter on the development of the microporosity. It is in the larger porosity that the differences manifest themselves. The more highly mineral-containing sample produces more large microporosity and mesoporosity.

It bears repeating that the demineralization can hardly be viewed as complete with this particular coal char, even if it is significant in extent. There does appear to be an effect of the mineral matter in the creation of smaller mesopores, which might be even more evident, were it possible to more completely remove the mineral matter.

Figure 24. The BJH isotherm analyses for the Illinois No. 6 char experiments shown in Figure 23. Carbon burnoffs and the demineralized samples are indicated in the legend.

The above results were all for gasification of the char in air (oxygen). The influence of

mineral matter on CO₂ gasification was also explored. The kinetics are shown in Figure 26. It is very well established that gasification kinetics in carbon dioxide are quite strongly influenced by catalytic agents in the mineral matter, and the present results confirm the influence.

Figure 25. DFT data on untreated and demineralized Illinois No. 6 char gasified in air (same conditions as Figure 23).

The samples of untreated Illinois No. 6 char could therefore be gasified at a lower temperature than the samples of acid-treated char. The Zone I gasification experiments with untreated char took place at a temperature of 1118 K (845° C), whereas the comparable experiments with the acid washed char required 1183 K (910° C).

Figure 27 presents data on the development of surface area in CO₂ for the untreated and

acid treated samples of Illinois No. 6 char. It is clear that, once again, that the untreated char develops surface area more readily than does the acid-treated (partially demineralized) sample. Again, at low burnoffs, the surface areas are quite comparable (as they were in air) and they then diverge as the burnoff increases.

Figure 26. The kinetics of gasification of Illinois No. 6 char in carbon dioxide at atmospheric pressure.

There is obviously a vast difference in the surface areas developed in air and CO_2 , for this particular char. This may be seen by comparison of the values in Figure 27 with those in Figure 23. Activation in air is much more effective for opening up the microporosity that is associated with high surface areas. This is true throughout the entire range of burnoffs selected for study. It should be recalled from Figure 10 that the temperatures of experimentation were selected such that rates in

both gases are comparable; this naturally required much lower temperatures in air than in CO₂.

The pore size distribution that develops during CO₂ activation may be examined using BJH analysis of the same isotherms as used in producing Figure 27. The results are shown in Figure 28. The pore size distribution that is developed is notably different than that seen in

Figure 27. The development of nitrogen BET surface area in Illinois No. 6 chars, gasified in carbon dioxide at atmospheric pressure. The gasification of the untreated sample took place at 1118 K while that of the partially demineralized sample took place at 1183 K.

Figure 24, for the gasification using oxygen. What is especially apparent is the development of a peak in the mesopore range. This was not seen in the air gasification of partially demineralized char, though there was some tendency in that direction in the case of the untreated char.

Figure 28. Mesopore size distributions developed during CO₂ gasification of partially demineralized Illinois No. 6 char. The char was gasified in atmospheric pressure CO₂ at 1183 K.

The comparison of BJH profiles for treated and untreated Illinois No. 6 chars gasified in CO₂ is shown in Figure 29. The development of porosity in the untreated samples is greater, consistent with what might be expected on the basis of Figure 27. Again, this is apparently associated with the effects of the mineral matter on porosity development in the indicated small pore size range, since the data are for the same range of burnoffs.

Figure 30 provides information regarding the development of porosity as provided by the DFT analysis. This analysis shows that there is significant development of microporosity at low burnoffs, but then the process shifts towards development of mesoporosity.

Figure 29. Comparison of the BJH pore size distributions for Illinois No. 6 chars gasified in CO₂.

The results in Figure 30 actually indicate that there is a fairly limited degree of micropore development at low burnoffs, and that it is mesopore-size pores that begin to develop first. After this, there is a very rapid development of both mesopores and micropores. It may be seen from the divergence of the higher burnoff curves at larger pore widths in Figure 30, that the process at high burnoffs favors the opening up of smaller mesopores. This is consistent with the results from the BJH analysis.

Figure 30. Partially demineralized Illinois No. 6 char gasified in atmospheric pressure CO₂, analyzed using DFT.

Figure 31 compares the development of porosity during CO₂ gasification in the untreated and acid washed Illinois No. 6 coal chars. Once again, it is very apparent that the acid washed material is unable to develop small porosity, on the micropore or mesopore scale, nearly as effectively as does the untreated material.

Figure 31. A comparison of the BJH results for untreated and acid-washed Illinois No. 6 coal char gasified in CO_2 .

There is a question as to whether the Illinois No. 6 that is acid-washed has created in it during pyrolysis less free volume that can be opened up, or whether it is really that the mechanism of gasification shifts to one favoring the development of pores outside the micropore and mesopore regions examined. It would appear that the more likely explanation is the latter, since the degree to which pores do open depends upon the gasifying agent (compare Figure 31 with Figure 25). Since it is clear that the development of smaller pores (micropores and mesopores) is less in the acid-washed sample, for any given degree of burnoff, it is clear that the burnoff must be taking place more in the largest range of pore sizes in the acid-washed sample.

Figure 32 shows the results of gasification rate experiments conducted in air on demineralized and untreated Wyodak coal chars. Once again, the role of catalytic impurities on the rate is immediately apparent. The rates of gasification are much higher in the presence of the minerals. Again, given how these particular experiments were preformed, it is not clear how much of an effect is due to differences in how the char set up (was there a catalytic effect at that point) as opposed to later, during the actual gasification.

Figure 32. Rates of reaction of untreated and demineralized Wyodak coal char in air. The untreated sample was examined at 15% burnoff, whereas the demineralized sample was examined at 0%.

The porosity development experiments were conducted as guided by the results of Figure 32. The temperatures for air gasification of the samples were selected so as to place the samples clearly within Zone I conditions. The results for development of BET area are shown in Figure 33.

Figure 33. BET surface area development in air, for demineralized and untreated Wyodak coal chars. The untreated char was gasified at 624 K (351°C), and the treated char at 717 K (444°C).

The development of surface area is less pronounced at low burnoffs, for the demineralized sample, just as in the case of the Illinois No. 6 char. Just as for the Illinois No. 6 char, the differences in development of pore surface area in air are not very large, by this measure.

The development of porosity in air is tracked using the DFT method in Figure 34. In this case, the development of microporosity is seen to lag in the demineralized samples, but eventually, the final chars are seen to be quite similar, irrespective of whether they contained the mineral impurities or not. There is even seen to be an initial pre-gasification difference in the pore volume

distributions of the two samples, but these disappear relatively quickly with a small amount of gasification. There also is what appears to be a limit in micropore development. Once this is approached, the main pore development takes place in the mesopore region.

Figure 34. The development of micro- and meso-pores in Wyodak chars gasified in air, analyzed by the DFT method. The gasification temperatures were as in Figure 33, and were in the Zone I regime.

Figure 35 displays the results for porosity development as examined using BJH theory,

which, again, has as its focus the mesopore region. These results confirm that the development of porosity on the mesopore scale in the demineralized sample lags slightly the development of porosity in the untreated sample, though at high burnoffs the results tend to converge. The differences in the shape of the curves for the untreated and demineralized samples is never particularly great, except that it appears as though the untreated sample might have somewhat more

Figure 35. The results of BJH analysis applied to the same isotherm data as were used in Figures 33 and 34.

porosity development in the large mesopore or small macropore range.

In contrast to the relatively modest effect of the catalytic minerals on the porosity of chars activated in air, the chars activated in carbon dioxide showed a considerably greater effect. The significant effect of the catalytic minerals on the reactivity of the Wyodak chars is shown in Figure

36. It should be noted that the reactivity in carbon dioxide is much lower than that in air, as is apparent from the comparison of the temperature scales of Figures 36 and 32. These reactivities have been examined in a range of temperatures over which the reactions still occur under Zone I conditions. Figure 37 shows results published earlier from this lab, showing the transition between two Zone I regimes [39]. In what has been described as the higher temperature chemisorption control regime of reaction, the untreated sample is always more reactive than the demineralized, whereas in the lower temperature regime desorption is believed to control and catalysts have no effect. The samples in this study were prepared under the chemisorption control regime of Zone I.

Figure 36. Reactivity of Wyodak coal char in atmospheric pressure CO₂.

Figure 37. A comparison of the reactivity of Wyodak coal char in 4.8 kPa of carbon dioxide under Zone I conditions. Closed points-untreated, open points- demineralized [39].

Figure 38 shows the usual result that the development of surface area in the demineralized sample is less than that in the untreated sample, given comparable levels of burnoff. It is not clear why the development of surface areas at very low burnoffs should be so much more rapid in the untreated sample than in the demineralized sample. On the one hand this would seem to suggest that the untreated sample has a great deal of open pore volume that can be readily opened and that this pore volume is not present in the demineralized sample. Such an explanation cannot be correct in light of the data of Figure 33, however. In the case of air activation, the porosity rapidly develops at low burnoffs in both the demineralized and untreated samples. The inability to rapidly develop this porosity in carbon dioxide must be related to a reduced ability to remove the blocking carbon in the absence of catalytic agents on the surface.

Figure 38. Comparison of surface area development in carbon dioxide activation of Wyodak coal char. The demineralized char was gasified in atmospheric pressure carbon dioxide at 1107 K, while the untreated char was gasified in 4.8 kPa of carbon dioxide at 1007 K.

The pore size distribution of the untreated Wyodak char is displayed in Figure 39, and that of the demineralized Wyodak char in Figure 40. The differences between the untreated char and demineralized char pore size distributions are quite clear, both in terms of the shape of the distributions as well as the magnitudes of the porosity.

Figure 39. Mesopore size distribution in untreated Wyodak coal char gasified in 4.8 kPa of carbon dioxide, calculated using BJH theory.

It is quite apparent that the untreated char develops much more porosity in the mesopore range, and that this has a characteristic size which is well defined to be roughly 30 Å in characteristic diameter (it should be borne in mind that the concept of “diameter” is an approximation to reality for this material, which is more likely to have slit-shaped pores). Hence the demineralized material appears to be gasifying in such a way as to not result in development of nearly as much microporosity or mesoporosity as develops in the untreated sample. What this must mean is that the removal of carbon from the demineralized samples takes place on such a size scale as to not be visible in these analyses- i.e., on a very large scale (macropores or superficial surface). It should be remembered that this inability to develop pores in this size range did not exist in the

case of activation of the demineralized char in air (Figure 35). Hence this aspect of porosity development is unique to the processes that determine carbon dioxide reactivity in the demineralized samples.

Figure 40. Mesopore size distribution in demineralized Wyodak coal char gasified in atmospheric pressure carbon dioxide, calculated using BJH theory.

Figure 41 presents a direct comparison of the data for treated and untreated Wyodak coal char gasified in carbon dioxide. By placing the data on the same scale, the very stark differences in the amount of porosity formation become more evident. Clearly, the acid treated sample is largely missing the mesopore peaks that are present in the untreated sample. The mechanism of formation of the preferred pore sizes is not established by these measurements, but there is no question that it is related to catalyst effects that in some way define a particular pore size.

Figure 41. A comparison of the mesopore size distributions in untreated and demineralized Wyodak chars gasified in carbon dioxide.

Figure 42 shows that the differences in porosity development in untreated and demineralized chars cannot be attributed to the difference in carbon dioxide partial pressures of the experiments leading to the results of Figure 41. Figure 42 once again shows that the demineralized sample develops a much less mesoporosity than does the untreated sample, and that the amounts of porosity development in the demineralized sample are not much influenced by the differences in carbon dioxide partial pressure. It is also notable that a char prepared at a much higher temperature tends to behave more like the demineralized sample. Earlier work in this laboratory has demonstrated that the CaO surface area of the samples drops rather precipitously with heat treatment, and is almost an

order of magnitude lower for the 1648 K char than for the 1273 K char [40]. Since alkaline earth minerals are suspected to be the main catalytic agents of interest in these chars, the reduced ability of the highly heat treated char to produce small porosity is consistent with the effects of demineralization. Both somehow shift the process of gasification to removal of carbon in such a way as to disfavor the uncovering of existing internal microporosity or creation of mesoporosity.

Figure 42. A comparison of pore size distributions developed in Wyodak coal chars gasified in 4.8 kPa of carbon dioxide. Comparison is made between the chars prepared at the usual 1273 K and one prepared at 1648 K.

Figure 43 compares the porosity developed in untreated and demineralized Wyodak chars, using DFT calculations. This figure confirms several features of the earlier presented features. There is clearly a greater ability to develop micro- and meso-pores in the untreated sample, that persists well into the mesopore size range beyond that shown in Figure 43.

Figure 43. Pore size distributions developed in untreated and demineralized Wyodak coal chars gasified in carbon dioxide, calculated using DFT.

Figure 44 shows the evolution of the pore volume in the demineralized Wyodak coal chars. There is a complicated pattern. There is initially some modest development of micropore volume, which does not continue until somewhat higher burnoffs are attained. The pore size distributions are relatively flat going into the mesopore region, indicating that mesopore development is not favored in these chars.

Figure 44. Development of porosity in demineralized Wyodak coal char, tracked using DFT. Burnoff levels are indicated on the figure.

Figure 45 shows that the reactivity of Wyodak coal char towards nitric oxide can also be affected by the presence of catalytic agents. Just as in the case of carbon dioxide gasification, in nitric oxide gasification, there is an effect of catalysis seen under Zone I reaction conditions, in which chemisorption processes control the rate. At the lowest temperatures shown in the figure (high values of $1000/T$), the process is not seen to be influenced by the presence of catalysts, consistent with the hypothesis that the process is desorption controlled under those conditions. A desorption process is much less likely to be influenced by the presence of catalysts than would be a chemisorption control process. This figure also shows for the untreated char the transition to the Zone II reaction rate regime, and with it, a decrease in slope of the rate curve, at high temperatures

(or lower values of $1000/T$).

Figure 45. The influence of catalytic minerals on the observed rate of Wyodak coal char gasification under a partial pressure of 0.82 kPa of NO.

Figure 46 shows a comparison of the mesoporosity developed in untreated and demineralized Wyodak char gasified in nitric oxide to comparable burnoffs of roughly 25%, under the Zone I chemisorption control conditions. The results are once again consistent with the fact that the presence of catalysts in the char favors the formation of mesopores of a certain size range, whereas their absence results in a pore size distribution that declines from the micropore size range through the mesopore range.

The above results leave little doubt that there is a catalytic influence of mineral matter on the subsequent activation of coal chars in oxidizing gases. It has been observed that there are measurable reaction rate effects of catalytic minerals on two very different chars (one prepared from a softening bituminous coal, the other from a non-softening subbituminous coal). The effects on rate are observed in three oxidizing gases- oxygen, carbon dioxide, and nitric oxide- whose reactivities span several orders of magnitude at any given temperature of interest.

Figure 46. Mesopore size distributions in untreated and demineralized Wyodak coal char gasified in 0.82 kPa of NO.

There is, along with the influence of the catalytic agents on the rates, a strong influence of the catalytic agents on the development of porosity. For comparable levels of burnoff, activation in oxygen (air) gave higher surface areas than did gasification in carbon dioxide. The observed differences in porosity development in untreated and demineralized chars was greater in carbon dioxide than it was in oxygen.

Generally speaking, the untreated chars showed more development of small porosity (and with it, surface area) than did the demineralized chars. The differences in pore size distributions could be modest (as they were in air or oxygen) or they could be quite large (as they were in carbon dioxide or nitric oxide). The fact that the development of porosity for a given char in air was somewhat similar, irrespective of the presence of catalysts, combined with the fact that porosity was always developed much faster and to a greater extent in air than in carbon dioxide, was taken as a sign that the carbon dioxide's action on the char was more affected by the catalysts, and that in their

absence, the carbon dioxide was much less effective in opening up both the small pores that exist in the char from the time of pyrolysis as well as the slightly larger ones (mesopores) that are created by carbon removal.

2.5 The Effect of Oxidizing Gas Pressure on the Activation of Coal Chars

It has already been noted above that the course of activation appears to be somewhat insensitive to the partial pressure of the oxidizing gas, within a moderate range of partial pressures. Further information is presented in this section in support of this view.

Figure 48 presents a rather typical Arrhenius plot of kinetic data obtained by gasification of Pittsburgh No. 8 coal char in 4 atm of carbon dioxide. There is apparently nothing remarkable about the kinetic behavior of the gasification processes if viewed over a modest range of conditions.

Figure 48. Kinetics of gasification of Pittsburgh No. 8 coal char in 4 atm of carbon dioxide.

Still, there is a relatively rich complexity of the gasification kinetics that simple analyses of

the above sort cannot reveal. For example, Figure 49 shows that the effect of carbon dioxide pressure itself follows no simple pattern.

Figure 49. Rate of gasification of Pittsburgh No. 8 coal char in carbon dioxide. In these experiments, the pressure was continuously increased. The experiments were conducted with fresh char and with char that had been earlier burned off to 15% mass loss. All experiments were conducted at 1209 K, $\pm$ 3 K.

The effect of pre-burnoff on the rate is apparent from the results of Figure 49, even though the scatter inherent in the data do not permit establishing exactly how large the effect is. A more interesting consequence of pressure variation was seen in experiments in which the pressure was deliberately changed in one direction or another. These results are shown in Figure 50.

When pressure is monotonically increased, the rate of reaction rises to an asymptotic value, just as was observed in Figure 49. When carbon dioxide pressure is, however, decreased over the same range, the rate shows an apparent negative dependence on pressure, over the high pressure portion of the curve. There was similar behavior noted in replicate experiments within the same general range of temperature. It is unclear precisely what the mechanism of the rate reversal is, and

this study was not concerned with its elucidation. What this does clearly warn of is the existence of competing processes whose paths do depend somewhat on previous sample history.

Figure 50. Gasification of Pittsburgh No. 8 coal char in carbon dioxide. The direction of pressure variation is shown in the legend. The experiments were conducted at 1216 K.

Within the context of such complexity, it would not be surprising to find pressure effects on the development of porosity. Still, as the results will show, these were not normally observed. Figure 51 displays the results obtained for the opening of porosity in the Pittsburgh No. 8 char at 4 atmospheres of carbon dioxide pressure. The behavior is unremarkable. There is the expected opening of micropores and small mesopores (the raw char gives a curve that is difficult to measure, because of its low porosity- it is coincident with the pore width axis). More indicative of the effect of pressure on porosity development is Figure 52, which compares the development of porosity in 4.8 kPa of carbon dioxide to that in 400 kPa.

It is readily apparent from Figure 52 that despite the almost two order of magnitude increase

in carbon dioxide pressure, the porosity development is quite similar. The development of surface area is naturally linked to the development of small pores, so it comes as little surprise that the surface area behavior with burnoff is also quite similar over a wide range of pressure (see Figure

Figure 51. Development of porosity in Pittsburgh No. 8 coal chars gasified in 4 atm of carbon dioxide at approximately 1200 K. Burnoffs are indicated in the legend. Curves are calculated from nitrogen isotherms using DFT methods.

53). These results again confirm that the basic character of the porosity in a given coal char is much more closely linked to the nature of the starting coal than to the conditions of activation of the char. Of course, the results above showed that the activating agent can play an important role in determining the extent and nature of pore formation, but once the combination of coal and activating agent are established, the most important factors are in place. The pressure of the activating agent is somewhat less important (provided that the processes are carried out in the same mass transfer

regime).

Figure 52. Development of porosity in Pittsburgh No. 8 coal char gasified in carbon dioxide at the indicated pressures to the indicated burnoffs. All experiments were performed under Zone I conditions.

2.6 Summary of Factors Influencing Porosity Development in Coal Chars

The above results have tended to reinforce and show on a quantitative basis what had been qualitatively understood for some time by those who seek to prepare carbons, by physical activation, from coals as raw materials. Namely, the first and foremost choice is that of starting feedstock. It is simply not possible to tweak activation conditions in order to create a highly porous carbon from materials that soften during carbonization. There are certain choices of activating conditions that will influence the amount of porosity formed, but the influence of these is decidedly secondary as compared with the influence of the starting coal itself. This report only briefly touched upon the issue of carbonization conditions as possibly influencing the nature of porosity. While high heat

treatment temperatures will generally produce more refractory carbons, it will also tend to drive the materials towards a greater degree of order.

Figure 53. Development of BET surface area in Pittsburgh No. 8 coal char gasified in carbon dioxide under Zone I conditions.

Of comparable importance to the nature of the carbons produced are the activating agent (oxidizing gas) and any mass transport limitations that might be encountered during the activation. These of course act through very different mechanisms. By crossing into Zone II diffusion limited conditions, the porosity in the carbon can never be as fully developed as it is under Zone I conditions. There is always a practical temptation to push reaction rates to maximum values, so as to increase throughput for any given activation system. This often rules out the use of oxygen in air as an activating agent, since there is too great a risk of thermal runaway or unintentional elevation of the temperature into Zone II conditions. In no case was it found that oxygen was inherently an

inferior activating agent. It is always reasonably good. it is simply difficult to use in practice.

Despite the similarity of the inherent reactivities of steam and carbon dioxide towards coal chars, there is little doubt that steam is the superior choice for activation. Steam generally provides a higher degree of porosity, comparable to that in oxygen mixtures, and has the advantage that it is an endothermic activating agent, and thus, inherently more controllable than oxygen. Carbon dioxide's performance is clearly influenced by the presence of catalytic agents. Of more academic interest is the efficacy of nitric oxide, another powerful oxidizing gas. Nitric oxide performs in a manner similar to oxygen, sometimes it is superior, and sometimes inferior, but always very close.

Naturally-occurring catalytic agents always influence porosity development to some degree. Their influence is seen with air, carbon dioxide and nitric oxide (steam was not systematically studied here). Generally, materials that have been treated to remove some of their catalytic components will produce surface area less readily than untreated materials. It is formation of micropores and smaller mesopores that appears to be most impacted by the presence or absence of these catalytic agents.

In our limited examination of the effects of activating gas pressure on porosity development, we found very little evidence of significant effect.

3.0 Issues Related to Surface Area Development in Coal Chars

3.1 Relationship of Surface Area to Reaction Rate

One of the issues noted in the above sections of the report as having an influence on observed char reaction rates is that of surface area development. There is one school of thought that holds that since reaction obviously occurs on the surfaces of a carbon, the only logical representation of inherent reactivities involves a unit surface area basis. There is a related school of thought that emphasizes the role of so-called “active surface area”, not total surface area, since attack of an oxidizing gas on the basal plane of a graphitic structure appears to be much less favorable, for many reasons, than attack on some imperfection or edge of such a structure. There have been many attempts to develop quantitative measures of active surface area. Finally, there are those in the combustion community, who despite accepting the obvious importance of surface processes, argue that until a more quantitative basis can be provided for correlations with surface area, expressing reactivity on a mass of carbon basis is at least as reliable, and requires less characterization of the material.

The results of the present study provide some insights into the question, since throughout much of this work, reactivity was being measured at the same time as was surface area. This section of the report presents some of the results from combining these results.

The course of reactivity of the Pittsburgh No. 8 char with burn-off is shown in Figures 54 and 55 for NO as a reactant. These results were obtained in the TGA device. The difference between Figures 54 and 55 is that in the case of Figure 54, reactivity is expressed as $(1/m_0)(dm/dt)$, where m_0 is the original sample mass, whereas in Figure 55, the reactivity is given as $(1/m)(dm/dt)$ where m is the instantaneous sample mass.

Again, the choice of NO as a reactant might appear initially to be odd, since this gas is not normally utilized either in activation or in combustion or gasification processes. The choice was,

however, guided by two considerations. One is that we have had extensive experience in examining the reactivities of carbons with this particular reactant as part of another study. Another reason is that NO represents an oxidizing reactant with an intrinsic rate intermediate between oxygen and carbon dioxide. It is neither as reactive as oxygen, which has the problem of creating thermal runaway conditions at low temperatures, nor as unreactive as carbon dioxide, which requires quite high temperatures for examining reaction rates.

The reactivities of chars derived from phenol-formaldehyde resin and pine wood are shown for comparison. These materials will not be discussed further here, except to say that the chars were prepared at comparable pyrolysis conditions. The results for these materials are shown to emphasize that much higher reactivities can be observed with other materials having comparable sample mass and particle size. The reactivity of the Pittsburgh No. 8 char is therefore not controlled by external transport limitations.

Figure 54. Reactivity of three different chars in nitric oxide. The reactivity measurements were performed at 1023 K in 0.8 kPa of NO. The reactivity is shown “normalized” by the original sample mass, m_o .

When the different reactivity bases of Figures 54 and 55 are compared, it is apparent that neither gives a consistently more constant reactivity than the other. Expressing the reactivity of Pittsburgh No. 8 char on either basis gives remarkably constant behavior over a wide range of burn-off; expressing the reactivity on a $(1/m)$ (dm/dt) basis gives a value which generally increases with burn-off after an initial decrease, whereas the $(1/m_0)(dm/dt)$ basis shows a decrease (to 2% burn-off), an increase to a maximum at around 12% burn-off and then another decrease thereafter. The changes in the reactivity with burn-off of the phenolic resin char and pine char are much more dramatic.

Figure 55. Reactivity data of Fig. 54, normalized by instantaneous mass m .

The differences in reactivity variation with burnoffs in the different chars can be put into some perspective by noting that both the phenolic resin char and pine char are thermoset chars, as opposed to the thermoplastic Pittsburgh No. 8 char. Hence, the surface areas of the phenolic and pine chars develop to a much greater degree than does the surface area of the Pittsburgh No. char. This point has already also been made in comparisons of the Pittsburgh char to the chars of nonsoftening coals.

The course of reactivity in carbon dioxide is illustrated in Figures 56 and 57, with the difference between these two figures again being the mass basis for displaying the data. Figure 56 shows the rate data normalized by the initial mass m_0 and Figure 57 shows the rate data normalized by the instantaneous mass, m . In the case of Figures 56 and 57, a comparison of the Pittsburgh No 8 data is shown only with the char derived from phenolic resin char, because the pine-derived char has a relatively much higher reactivity than these other two materials and cannot conveniently be represented on the same linear scale.

Figure 56. A comparison of the reactivity behavior of Pittsburgh No. 8 coal char and phenolic resin char in carbon dioxide at 1123 K and 8 kPa pressure. The reactivity is shown “normalized” by the original sample mass, m_0 .

The course of reactivity in oxygen is shown in Figures 58 and 59. In this case, the Pittsburgh No. 8 char shows a higher reactivity than does the phenolic resin-derived char. The curves of reactivity variation with burn-off show a very dramatic curvature, not evident in the case of reaction in NO or CO₂. These results suggest very strongly that a universal reactivity profile should not be expected - that is, the model of how surface area develops and how this affects reactivity, will be quite different in the three cases. It is also interesting to note that in all cases, the combination of temperature and reactant gas concentration were chosen so as to provide a comparable rate of reaction, at least initially. This may be verified by comparing the ordinate scales of Figures 54, 57 and 58.

Figure 57. Reactivity data in CO₂, of Fig. 56, normalized by instantaneous mass m.

Focusing for the moment on the representation of data involving normalization by m_0 (Figures 54, 56, and 58), it appears that over a wide range of burn-off, the rates in NO and CO₂ are quite constant with burn-off, whereas the rate in O₂ increases and decreases dramatically. This is emphasized by the comparison in Figure 60, which illustrates the change in rate with conversion in each gas, normalized by the rate at 10% conversion. This permits a convenient viewing of all of the data on the same plot. The results of Figure 60 might be taken to suggest that the reactive surface presented by the solid does not change much with burn-off in the NO and CO₂ cases, whereas it does so dramatically in the case of O₂

Figure 58. A comparison of the reactivity behavior of Pittsburgh No. 8 coal char and phenolic resin char in oxygen at 773 K and 2 kPa pressure. The reactivity is shown “normalized” by the original sample mass, m_0 .

The behavior seen in the case of oxygen is often reported in the literature [8-11, 41, 42]. The

general interpretation is that the surface area for reaction initially increases with burn-off, and then is lost as a result of pore coalescence. In one study [8], the patterns of porosity development were shown to depend upon the combination of reactant gas and char, but were independent of temperature and reactant gas concentration. Based upon our results, we concur that the choice of temperature and reactant gas concentration should have little effect, provided that operation remains under Zone I conditions.

Figure 59. Reactivity data of Fig. 58, in O_2 , normalized by instantaneous mass m .

Differences in variation of reactivity with burn-off for O_2 and CO_2 have been noted previously [8]. In that earlier study, the patterns exhibited by another Pittsburgh No. 8 char during carbon dioxide and oxygen gasification were qualitatively similar to those shown in Figures 56 and

58, respectively, but the maximum in the CO_2 reactivity was more pronounced. That study also emphasized the importance of starting material in determining the behavior; an Illinois No. 6 char gave very different behavior in the two gases. Again, this is fully in accord with our results.

These observations led to a conclusion that micropore area might not be fully utilized in the case of oxygen gasification [8]. The possibility that there is an inability to fully utilize micropores has been cited by many workers in the field [3-5, 7,11]. The evidence has generally been somewhat indirect, however, and the issue must still be regarded as open. Unfortunately, the results of the present study also cannot shed light on this question, since it is apparent that micropore opening does occur in many cases, though it is unclear that it really does involve actual penetration of the structure by the reactant gas.

Figure 60. Reactivity of Pittsburgh No. 8 coal char in various gases as a function of conversion (burnoff).

From the above results, all of which were obtained under what were believed to be intrinsic reaction rate controlled (the “Zone I”) conditions, it can be seen that great care must be

exercised in defining the conditions of reaction. The patterns of reactivity, and therefore porosity development and use, would be expected to be quite different in the case of these three reactant gases.

Even when an attempt is made to “normalize” reactivity by available BET surface area, the patterns of reactivity are different. This may be seen in Figure 61.

Figure 61. Reactivity of Pittsburgh No. 8 coal char in three different oxidizing gases, expressed as a rate per unit BET surface area. Since these rates differ for the three gases, they are further normalized to a basis of unit reactivity at approximately 10% burn-off.

It appears to be the case that the BET area is a reasonable normalizing parameter for reactivity in oxygen, but not in NO or CO₂. The implication of an apparent rise in reactivity at high conversions could be that the original surface area provided an over-estimate of the surface area accessible to a reactant. This might happen as a result of an increase with conversion in accessibility of pores counted in surface area.

We have explored various other measures of pore surface area or volume (e.g., mesopore

volume) with which to correlate reactivity. None has proven more satisfactory than that based upon BET surface area. Again, it is not proposed that the micropores can actually be penetrated by the reactants. Rather, the BET area is a measure that correlates with surface roughness, or the number of places that a reactant gas can “find” to react with the carbon. We now know of the results such as those in Figure 21, showing that there is less development of microporosity and mesoporosity under Zone II conditions. Results such as those in Figure 20 remind us of the fact that while there is loss of about half of the mass of the carbon in the system under Zone I conditions, volumetrically, this represents only of order 0.1 cc/g. Taking the density of carbon to be of order 1 g/cc, the amount of mass that must be removed to create the volume found in small pores is only a small fraction of total mass loss. The conclusion must be that mass is being generally removed from larger domains that entirely disappear, and only slowly do pores open in the remaining domains. The conclusion is that the mass transport that limits reaction might well be taking place on a scale much larger than the pores that are being developed. Hence, there is not necessarily any fundamental significance to a correlation with BET surface area.

3.2 The Issue of the Preferred Adsorptive

It was shown previously [7] that many conclusions regarding the development of porosity in coal chars could be strongly influenced by the choice of adsorptive; following the line of investigation suggested in [18], it was demonstrated that nitrogen was a better general adsorptive probe than carbon dioxide. It has often been noted to be the case that CO₂ gives higher apparent surface areas (micropore volumes) than does N₂ at low burnoffs. Figure 62 shows the comparison of the results obtained using these two adsorptives on chars that had been gasified in three different gaseous environments. This plot emphasizes the low burnoff regime.

The zero burnoff value for the CO₂ adsorptive is significantly higher than that for the N₂ adsorptive, but the former value is quite near that which the N₂ values quickly assume. It is unreasonable to believe that there takes place some special process by which pores that can be

examined by nitrogen, but not carbon dioxide, are created only at very low values of burnoff. Since diffusional limitations have already been concluded to exist at nitrogen adsorption conditions, it is more likely that what is responsible for the convergence of the nitrogen and carbon dioxide results is the loss of the diffusional limitations with limited amounts of carbon removal.

Figure 62. The BET surface areas of Wyodak subbituminous coal chars gasified in O₂ (717 K, 2.02 kPa), NO (911 K, 0.82 kPa), and CO₂ (1007 K, 4.80 kPa), measured using CO₂ adsorption (open points) and N₂ adsorption (closed points).

Thus it seems that the microporosity that is apparently "created" mostly already exists and that it is indeed hindered diffusion of N₂ into small pore openings that is the source of an artifact at 0% burnoff. Microporosity is equally well characterized by both adsorptives at just above 0% burnoff. At this stage, there is no difference in porosity development in different reactants. Thus it appears that roughly 400 m²/g is an intrinsic initial value for this char, accepting as usual the fact that the BET model is only a crude indicator of microporosity. These data also support the view that all of this porosity is already present at the end of pyrolysis and it is unnecessary to base a model

of the porosity development due to carbon removal processes on these low burnoff results. Instead, these processes probably involve very subtle relaxation of the structure to some very limited degree, allowing the easier penetration of the nitrogen adsorptive. It would not be particularly surprising if protruding carbon atoms at pore mouths were the locus of initial chemical attack relatively independently of nature of reactant.

It is, however, clear that when the same samples are tracked to higher burnoffs, the effects of reactant gas begin to show themselves (see Figure 63). The question is what determines the very different patterns in the different gases at higher burnoffs.

Figure 63. The data of Figure 62, extended to higher burnoffs.

In Figure 63, the already documented inadequacy of CO₂ as an adsorptive probe shows itself clearly [7]. The nitrogen BET results show a rise to some limiting values of surface area, and

only at very high burnoffs in one case is a decline seen. It should be noted that these are results calculated to a gram of carbon basis, exclusive of the ash content. Since the ash content of the char is essentially non-porous, to not recalculate to a carbon basis provides a misleading picture of how the porosity in the carbon portion is behaving; this latter point has been overlooked in some of the published literature on this topic.

Figure 63 shows that there is an apparent loss of porosity at fairly low burnoffs when the chars are examined using carbon dioxide as the adsorptive. Again, this phenomenon is well-known [7] and attributed to the inability of the carbon dioxide to fill the larger micropores, for reasons of thermodynamic instability of the condensed phase. On this basis, the decision was made in this project to use nitrogen as the primary adsorptive for characterizing the chars.

The above trends are not always observed. For example, consider the data of Figure 64 for the activation of Pittsburgh No. 8 coal char in air. These data show that the carbon dioxide and nitrogen BET results track each other fairly closely. It is important to note that the samples at each burnoff are identical, so the variability in results can only be attributed to the differences from use of nitrogen and carbon dioxide adsorptives (this is also why the same BET working equation was used for carbon dioxide as for nitrogen, so as to avoid differences related to use of different theories).

Figure 64. Nitrogen and carbon dioxide BET surface areas of Pittsburgh No. 8 chars activated in air. The carbon dioxide work was performed at 195 K.

What the above comparison of results shows is that there is not a universal ability of carbon dioxide to penetrate pores that nitrogen cannot. In the case of the Wyodak coal char, as in the case of many other disordered carbons, the difference is seen. In the case of the Pittsburgh coal char, the difference is trivial at the outset, and never gets very large. The danger that carbon dioxide will miss some larger pores that the nitrogen can interrogate will outweigh any perceived advantage that the carbon dioxide might have in interrogating restricted narrow pores, which is only an issue at low burnoffs.

3.3 The Examination of Unburned Carbon in Coal fly Ash

This project has been concerned with the factors that determine the development of porosity in chars derived from coals. The porosity is an essential characteristic of activated carbon products.

Char porosity and surface area however also play an important role in combustion (or gasification) of coals. For both reasons, it was of some considerable interest to see how the porosity is affected by various factors associated with pyrolysis, combustion, or gasification. In this section, the focus is mainly on the development of porosity in combustion, or combustion-like, environments. The intent is to explore how this clarifies how certain variables can affect the development of porosity.

Practical char combustion processes can be at least partially pore-transport controlled, even in pulverized coal firing [1]. Moreover, much literature suggests that char reactivities should be expressed on a surface area basis [2], although small char micropores might not be fully utilized during oxidation or gasification [e.g., 3-8]. Many models have been proposed to describe development of char surface areas with burn-off [9-15], but many features need further clarification - e.g., different patterns of porosity development are observed in the same char, in different gases, even when rates of reaction are set to be identical [7, 16].

It is difficult to obtain direct information on the mode and mechanism of char combustion in full-scale flames and furnaces. The work performed here provides insight into the question of porosity development in combustion by comparing pore structures of char residues from full-scale furnaces with the pore structures developed by coal chars burned in the laboratory under a variety of conditions, including true Zone II conditions. This allows comparison of the effects of two important variables - heating rate and temperature.

3.3.1 Kinetics of Gasification in Oxygen

Figure 65 shows kinetic data obtained for burning all eight Premium Coal chars in air. The results are expressed as the mass loss rate per remaining mass, $dm/dt \cdot (1/m)$. The techniques employed in this case were the same as those used throughout this report, so there is no distinction between “burning” and “activation” in this case. All of these experiments represent conditions under which the samples were carefully kept under thermal control, and so remained under Zone I

or Zone II reaction conditions. This will not be the case with some other samples discussed below.

Because the interest here centers on actual combustion-derived chars, these were examined as a source of very highly activated carbons. Therefore, Figure 65 shows results obtained on a bituminous coal-derived fly ash carbon for comparison. There is often a problem in more precise characterization of utility-source chars because of frequent fuel switching at the utilities. Hence, the precise identity of the parent coal for this char was unknown, as is typical of commercial fly ash samples.

Figure 65 shows a very common trend that reactivity decreases with increasing rank of parent coal, as has been observed in many other studies. The fly ash carbon sample exhibits reactivity that is similar to that of the Pocahontas char. This does not necessarily mean that the original coal in the case of this char was comparable in rank to the high-rank Pocahontas. The char that is left behind might well be a less reactive fraction of the original char that survived precisely because it was less reactive. Alternatively, this fly ash carbon also had a significant opportunity to thermally “anneal” due to the high temperatures that it probably experienced in the boiler. Many factors can influence the reactivity of a coal char, including composition/rank [e.g., 20, 21] maceral composition [e.g., 22], heating rate [e.g., 23], thermal annealing [e.g., 24] and the presence of catalytic matter [e.g., 25-28]. The observation of similar reactivity is therefore interesting insofar as it suggests that these factors are not fundamentally altered or overridden by the processes that take place during the achievement of high burnout- the sample from the fly ash is similar to an ordinary lab char.

Figure 65. Kinetics of oxidation of laboratory chars and fly ash carbons in air. Calculated Zone I activation energies are shown in the legend.

The other notable feature in this plot is that the results for the fly ash, Pittsburgh No. 8, Illinois No. 6, Blind Canyon and Lewiston-Stockton all show a distinct curvature in the direction of lower activation energies at high temperatures. Again, this is typical of a transition into a transport-controlled regime. The activation energies for the high temperature portions of the Arrhenius plots are 56 kJ/mol for the fly ash sample, 80 kJ/mol for the Pittsburgh No. 8 and 75 kJ/mol for both the Illinois No. 6 and Lewiston-Stockton samples. The latter values are quite close to the theoretical prediction for internal pore diffusion-limited kinetics (Zone II conditions), under which the observed activation energy becomes approximately half of the true activation energy. This afforded an opportunity to observe the development of porosity in these chars under pore diffusion-limited

conditions.

3.3.2 Porosity in Utility Fly Ash Chars

The BET surface areas of residual char in fly ashes have been measured by us for many samples provided by U.S. utilities. The results are shown in Figure 66, as a function of char micropore volume.

These values were obtained by difference from adsorption isotherms of the as-received ashes and the ashes with the carbon removed by combustion in a laboratory furnace. The calculations of BET area and micropore volume, from Dubinin-Radushkevich (DR) theory, followed the standard methods [33]. Figure 66 shows that all of the bituminous coal-derived carbons cluster in a narrow band of surface area from 20 to 80 m²/g-carbon, and contain only a modest amount of micropore volume. On the other hand, the low rank coals all exhibit higher surface areas, up to 400 m²/g-carbon. There is a good correlation between surface area and the micropore volume, since pores of small size often dominate surface area. It is worthwhile noting that this same relationship between coal rank and amount of micropore surface area was noted throughout the first part of this report. It is impressive that this survives to the very end of the burnout of these materials, showing how the notion of imprinting survives regardless of how much activation or burning of the char is done.

Figure 66. BET surface areas for bituminous chars (circles), and subbituminous or lignite chars (squares).

The small difference in the slopes of the correlation lines for the bituminous and low rank coal chars in Figure 66 shows a greater contribution of larger pores to surface area in the latter chars. This is because there are more mesopores, from 2 to 50 nm size, in the low rank chars. This may be seen more clearly in Figure 67, which displays the fractions of porosity in each of the pore size ranges. For the purposes of preparation of this graph, micropore volumes were calculated from DR theory, as described above. Mesopores were taken to be the volume of porosity calculated from the adsorption isotherm to 0.95 relative pressure, less the micropore volume. The macropore volume was taken to be the volume of pores from the relative pressure limit of mesopores to a relative pressure of 0.99. The class designations actually refer to the fly ashes from which the carbons were obtained, but they have a close correspondence to the ranks of the starting coals. Class C samples

are those obtained from lower ranks (lignites and subbituminous coals) and class F samples are those obtained from higher ranks of coal (bituminous).

Figure 67. The nature of porosity in coal chars in fly ash samples from utilities. Class F refers to bituminous coals and class C to lower rank coals.

What Figure 67 demonstrates is that the chars from bituminous coals generally contain lower amounts of total porosity than do those from the low rank coals. The actual distribution of porosity shows the same broad range in chars from both types of coals. This figure also makes clear that while there might be some bituminous coal chars that develop a fair fraction of

microporosity, the total amount is always small in comparison with that in the lower rank coals. Also, there is a significant portion of chars from bituminous coals (class F) that do not develop much microporosity at all. This is never the case for low rank coal chars.

Figure 67 is of course for samples of chars that have seen extremely high burnoff, but as a reminder of how these results tie to those presented earlier, we can consider the results of Figures 68 through 71. Figures 68 and 69 compare the DR micropore volumes in the chars prepared from Pittsburgh No. 8 bituminous coal and Wyodak subbituminous coal. The former should correspond well with a class F material, whereas the latter corresponds with a class C material.

Figure 68. Development of Dubinin-Radushkevich microporosity in Pittsburgh No. 8 coal char, under the indicated activation conditions.

As can be seen from Figure 68, this coal char appears to develop roughly 0.035 cc/g-carbon at higher burnoffs in oxygen. Keeping in mind that the burnoffs involved in the chars of Figure 67

are all well in excess of 99%, the results cannot be directly compared. Nonetheless, a crude comparison is possible. Taking from Figure 67 a typical total porosity for class F-type chars (0.07 cc/g-carbon) and a typical microporous fraction of 0.5, the product of these (0.035 cc/g-carbon) compares reasonably with what is observed in the laboratory char of Figure 68.

Figure 69 presents the same type of results for a char from the Wyodak subbituminous coal. It may be immediately observed that the microporosity is much greater for this char than for the char of Figure 68. By the same type of calculation as performed for the bituminous coal char above, it may also be seen that the micropore volume in this laboratory material is in the range typically observed for class C materials.

Figure 69. Development of Dubinin-Radushkevich microporosity in Wyodak coal char, under the indicated activation conditions.

Figure 70 shows the mesopore volume developed in the Pittsburgh No. 8 bituminous coal

char. In this case, the mesopore volume in the laboratory char falls towards the high side of what is seen from the utility chars, but is by no means out of the typical range.

Figure 70. Development of mesoporosity in Pittsburgh No. 8 coal char, under the same activation conditions as in Figure 68.

Figure 71 presents the mesopore information regarding the Wyodak coal char, as activated under laboratory conditions. It may immediately be seen that this lower rank coal char develops much more mesoporosity than does the higher rank coal char discussed above. In fact, the amount appears to be beyond what is typically seen for the utility chars of Figure 67, except that the char produced under Zone II laboratory conditions begins to resemble the utility chars. There is a very good reason for this, related to the nature of combustion in utility boilers, which will be explored further below.

Figure 71. Development of mesoporosity in Wyodak coal char, under the indicated activation conditions.

Referring again to Figure 66, the narrow range of surface areas seen in chars from a great variety of commercial pulverized combustion systems burning a great variety of bituminous coals raised a question as to whether there is apparently a fundamental limit on surface areas under these conditions. This narrow range was observed for fly ashes that had only a few percent up to those with over 30% residual carbon, so the observation did not depend upon the level of burnout, over a wide range.

Samples of fly ash chars were systematically combusted in the TGA device at experimental temperatures selected to provide Zone I conditions, under which maximum surface area development could be expected [7]. The results, expressed as BET surface area *of the carbon* are shown in Figure 72. Again, these experiments involved burning chars that had already seen 99+% burnout in utility boilers; the burn-off in Figure 72 is relative to this already highly burned-off state.

The inorganic non-combustibles in the ash had a relatively constant surface area of 0.7 to 0.8 m²/g and contained no microporosity; their small contribution was subtracted in calculating the carbon surface areas.

Figure 72. Development of surface area during laboratory combustion, in air, of chars from utility fly ashes. Fly ashes 22 and 74 come from bituminous coal combustion, and fly ash 75 from a subbituminous coal.

Results in Figure 72 were obtained on two different size fractions from two different bituminous coal chars (fly ash samples 22 and 74). Neither the surface area results nor kinetics (not shown) depend upon particle size under these particular reaction conditions, demonstrating the absence of transport limitations on the particle size scales examined here. When low rank fly ash chars are burned off under Zone I conditions (see results for fly ash 75), they likewise exhibit an increase in surface area, but to a much higher value.

The results of Figure 72 indicate that increased carbon surface area is possible, even in

highly burned out chars obtained from utility boilers. Thus, no “fundamental” surface area limit has been achieved in the boilers. Rather, the final surface area depends upon the conditions under which the combustion took place.

3.3.3 Surface Area Development in Laboratory Chars Under Zone I Conditions

The patterns of surface area development in laboratory-prepared chars have been presented earlier in this report. Again, oxygen partial pressure variations from 1 to 21 kPa did not influence these results, so there was not much concern about the influence of this variable in comparisons with utility chars (prepared in environments in which the oxygen partial pressure is well below ambient values as combustion is completed in the upper reaches of the boiler).

Figure 73 recaps the earlier presented surface area development in oxygen, for the full set of Argonne coal-derived chars. All surface areas increase with burn-off, at least initially. The ultimate extent of surface area development in the medium- and higher rank high- volatile bituminous coals (Pittsburgh No. 8, Lewiston-Stockton and Upper Freeport) is in the same range as for utility chars. The low volatile bituminous coal (Pocahontas) reaches somewhat lower surface areas than do the preceding lower rank coal chars. On the other hand, the lowest rank bituminous coals (Blind Canyon and Illinois No. 6) reach much higher surface areas. The two low rank coals (Beulah lignite and Wyodak subbituminous) achieve surface areas that are comparable to those observed for utility chars derived from low rank coals (see Figure 66).

Several of the coal chars exhibit a steep increase in surface area with burn-off, near zero burn-off (the fresh char state). Again, this behavior is well-known [e.g., 7], and as just discussed in the previous section of this report, attributable to an artifact of the measurements, having to do with nitrogen diffusional limitations at 77K [7, 18]. Figure 74 compares the ratio of surface areas for Beulah and Wyodak chars, using both nitrogen and carbon dioxide, and again shows that while nitrogen might underestimate fresh char surface area by a factor of two in these chars, the difference

rapidly disappears and already at modest burn-offs, nitrogen provides a higher estimate of surface area (and porosity).

Figure 73. Development of surface area during combustion in air of laboratory coal chars. The temperature of combustion is indicated.

Hence, any comparisons that are performed between the laboratory chars and utility produced chars should be made using nitrogen, and not carbon dioxide, as the adsorptive. The use of nitrogen will avoid questions regarding the ability to interrogate large porosity, which becomes of considerably greater relevance as burnoff reaches high values.

Figure 74. Comparison of N₂ and CO₂ BET surface areas for two coal chars.

3.3.4 Surface Area Development in Laboratory Chars Under Zone II Conditions

Porosity development was examined in experiments with samples that showed a transition from Zone I to Zone II in Figure 65. The Illinois No. 6 and Pittsburgh No. 8 samples were examined at temperatures very close to the transition. Figure 75 shows that both samples exhibited the expected shifts towards lower surface area development under Zone II conditions. The Beulah lignite char was also examined under Zone II conditions, but at a reduced oxygen partial pressure of 1%. The same behavior was observed. This sort of behavior has been previously noted in gasification of a low rank coal char by NO [7]. Because oxygen cannot fully penetrate char porosity under Zone II conditions, it is unable to develop porosity within the particle interior.

Figure 75. A comparison of porosity development in laboratory chars under Zone I (filled symbols) and Zone II (open symbols) conditions.

3.3.5 Implications Regarding Utility Boiler Chars

The preceding observations suggest the possibility that laboratory Zone I burning increases the surface area of the utility chars because these samples did not burn under Zone I conditions in the boiler. It cannot be stated with certainty whether the utility chars burned under Zone II or Zone III (external mass transport-control) conditions in the boiler, though the magnitude of the surface areas suggest the former- they are higher than those of fresh pyrolysis chars, and the very low areas of fresh pyrolysis chars would be maintained under Zone III conditions because oxygen cannot access any porosity. It has also been previously concluded, based upon other evidence, that Zone II

is likely the dominant mode in pulverized coal combustion [1,21].

Pore size distributions of samples obtained under different combustion conditions helps shed light on the processes. Figure 76 shows a comparison of the smaller range of pore sizes (micropores and small mesopores) developed in a number of very different samples. The results are displayed as cumulative pore size distributions calculated from density functional theory (DFT). The calculations were, as usual, performed using an integration kernel for nitrogen on carbon provided by Quantachrome Corporation. In addition to results for the same two fly ash carbons and Pittsburgh No. 8 coal chars already discussed above, the plot also features data obtained from combustion of a Pittsburgh No. 8 coal sample in a laboratory flat flame burner [43].

The results for the boiler and flat flame burner samples show a remarkable degree of similarity, especially since these coals burned in very different environments. These latter combustors gave chars that were obviously very different than the laboratory chars. The fresh laboratory char is much less porous, and the high burn-off laboratory char is much more porous than the boiler and burner chars. Even a low burn-off laboratory char, though showing a similar extent of porosity to the latter, shows a very different nature (more microporous). The laboratory char produced under Zone II conditions shows character most like the actual combustion chars. This char had been burned off to 11.9% extent, and its content of microporosity is lower than that for the 2.9% burn-off Zone I laboratory char, despite its considerably higher burn-off.

Figure 76. Cumulative DFT pore size distributions in the micropore/small mesopore region for utility chars, a flat flame burner (FFB) char and laboratory char, burned off to varying extents.

While the evidence presented above is not definitive proof of the boiler chars having been created under Zone II conditions, it is strongly suggestive of this. Such a pattern porosity development is not necessarily universal in practical combustion systems. For example, much less development of BET surface area has been reported for an industrial flame [44]. In that study, chars from several bituminous coals were found to develop BET surface areas of a few square meters per gram (maximum $13 \text{ m}^2/\text{g}$). Such results suggest Zone III-type of behavior, under which internal surface area cannot develop. On the other hand, the same coals gave chars which in a plug flow reactor developed surface areas in the more usual range of 30 to $80 \text{ m}^2/\text{g}$. Clearly surface area development depends upon combustion conditions.

3.3.6 The Development of High Microporosity

The very rapid apparent rise in BET surface area at low burn-offs (Figure 73) is often paralleled by a rapid, though less dramatic, rise in CO₂ surface area (see Figure 5 or other studies [e.g., 7]). Both argon at 77K [7] and benzene at 298K [45] also show sharp increases with initial burn-off so that large increases are not specific to nitrogen. The small difference in critical radii of N₂ and CO₂ cannot explain large difference in pore accessibility leading to large differences in surface areas, so the effect is usually attributed to slow activated diffusion of N₂ in adsorption at 77K [18].

The observed rapid initial increase in BET surface area is likely associated with a rapid increase in nitrogen access to *existing* microporosity at low burn-offs. This conclusion is supported by recent small-angle neutron scattering (SANS) results [46,47] showing a large amount closed-off internal microporosity, which can be opened at low extents of gasification in the Wyodak char [47]. The Pittsburgh No. 8 char has a lower level of pre-gasification closed porosity [46], consistent with its much lesser ability to produce high surface area materials. Still, there is some such porosity, and we believe that it is “opened” in the same manner.

A mechanism involving “uncovering” of existing microporosity appears responsible for the rapid initial development of surface area with burn-off. The covering that is removed must be fairly imperfect, as CO₂ can diffuse through it, to some extent. An argument based upon preferential removal of *strategically* placed carbons, blocking micropore mouths, is difficult to rationalize. Rather, it seems more likely that there is a general covering of the char surface by an imperfect blocking layer of carbon whose removal early in the gasification process enables nitrogen to access the porosity to which only CO₂ had access prior to its removal. Based upon examination of high resolution transmission electron micrographs [48], it appears as though there could exist a

very thin surface layer of ordered carbon at the surface of the char. The layer is most evident in the less-ordered carbons from low rank coals and it cannot be more than a few molecular layers thick. The “ordering” of this layer exists only in the sense that it presents the basal plane of graphitic crystallites to the interface. It may be speculated that this orientation at free surfaces is a necessary consequence of surface energy minimization (edge site minimization) during carbonization. The development of such a layer could be facilitated by the cracking of pyrolysis species - such cracking of hydrocarbons on surfaces always provides a layer whose orientation is parallel to the substrate. The layer must be imperfect, as it must present a significant impediment to nitrogen access at 77K but allow some access of CO₂ at the higher temperatures involved in adsorption of that gas.

If, for example, 1 m²/g is located in meso- and macro-pores (or on the external surface) of a given char, then the burning off of a layer of order of 10Å from this surface would involve the order a few tenths of a percent mass loss (taking as the density of the carbon a value of order 1-2 g/cc). Once the surface layer is burned off, the fundamental underlying pore structure of the carbon would continue to reveal itself throughout gasification, and that the micropore structure would no longer evolve, unless micropores are created as opposed to uncovered. This picture is supported by the burn-off results for a low rank fly ash carbon, in Figure 77.

Figure 77. Cumulative DFT pore size distribution for a utility char prepared from fly ash 75. The extent of additional laboratory burn-off is indicated.

In the micropore region, below 20Å, there is very little development of new porosity after a low extent of burn-off. Surface continues to evolve on the mesopore scale, though. Figure 76 suggests, though, that removal of a few tenths of a percent of mass is not necessarily sufficient to assure that the ultimate micropore content is fully exposed - the Pittsburgh No. 8 laboratory char with 2.9% burn-off has clearly not yet developed its full micropore structure. It remains unclear at present whether there is actual micropore creation in this sample.

It is, again, the inability of oxygen to fully penetrate char pore structure under Zone II conditions that prevents full opening of the microporosity, as already discussed in connection with Figure 76 for the laboratory Pittsburgh No. 8 char.

3.3.7 Summary

Thus, porosity development in laboratory chars, under Zone I conditions, follows trends determined mainly by rank. The development of porosity under Zone II-type conditions involves much lower increases in surface area (microporosity) with burn-off, as compared with Zone I conditions.

A comparison of the nature of laboratory chars with chars from utility boilers strongly suggests that the latter have been produced under Zone II-type conditions. The Zone II combustion conditions do not permit full opening of existing microporosity in the solid.

Nitrogen is a more reliable porosity probe than carbon dioxide, particularly at high burn-offs. It is believed that the initially very rapid apparent growth of nitrogen surface area (and more modest growth of carbon dioxide surface area) could be due to the removal of a surface layer that hinders access of both gases, but especially nitrogen, to existing micropores in the solid. Following the removal of this impeding layer, a relatively constant amount of micropore volume per mass is often revealed, as the solid recedes. The surface layer hypothesis requires more experimental verification, but it brings together many experimental observations in a self-consistent manner.

4.0 Final Conclusions

This project began with the belief that there was a need for a more systematic study of how coal chars develop porosity. This porosity is an important factor in determining the potential utility of activated carbons that might be derived from such chars, and is important in its own right in determining, and understanding, the kinetics of reaction of coal chars with oxidizing gases. There was a belief that perhaps by a more systematic exploration of the factors that control porosity development, it might be possible to tailor conditions to produce the desired char porous characteristics.

The results of this study have indeed confirmed the belief that certain factors can and do play an important role in determining the nature of porosity in carbons. The choice of reactant gas and the role of catalytic agents have been seen to have not insignificant effects on the type and amount of porosity created. What has, however, been far more impressive is the vital role that the starting coal structure plays in determining the nature of porosity. This variable is far more important than any other. It was seen, in section 3 of this report, that chars prepared from similar coals retain similar properties even when the heating rates in their preparation vary over several orders of magnitude, from the few degree per second of the laboratory oven to the tens of thousands of degrees per second of a utility boiler. The same may be said of the relatively minor influence of temperature of preparation over a wide range of conditions, from those near 1000°C in the lab furnace to what might be 1800°C in a utility boiler. And the same may be said of the burnoff of the char, ranging from some tens of percent in the laboratory to 99.99% in a typical utility boiler. Nature imprints a certain character upon the material, and it is difficult to steer this in a different direction, using ordinary pyrolysis and physical activation methods.

This study has presented, to our knowledge, the first systematic study of the effect of a wide range of activating gases on well-characterized coal chars. The results have indicated differences attributable to the combination, but again, what came out of the results spoke more to the similarity

of the results than the differences. The use of oxygen and steam appears to provide the greatest degree of activation for any given level of burnoff. The use of oxygen has, as its major drawback, the exothermicity of the activation reaction. This carries with it the danger of uncontrolled rise in temperature, which is not only a safety concern but which also threatens to move the process unintentionally into Zone II mass transfer control, which greatly reduces the potential for pore formation.

This study has also presented the first results that we are aware of regarding the comparison of porosity development under Zone I and Zone II conditions. It has been instructive in indicating that utility combustion chars have been formed under the latter conditions, consistent with other hypotheses along these lines.

It is hoped that this study will be of use in guiding future examinations of these phenomena. Some avenues of exploration were clearly not touched upon here. For example, here the emphasis was purely on oxidizing gases. The possibility of using reducing gases, such as hydrogen, to produce porosity has historically been examined to a much lesser extent, since it carries with it much less practical importance. It is also unclear that use of hydrogen or any reducing gas could do much more than the oxidizing gases to overcome the significant imprinting of the structure by the starting material.

Obviously, greater exploration could be made of the use of catalysts for tailoring porosity. In this study the examination was admittedly crude, though it certainly pointed to the limitations that are imposed by the choice of starting material and activating agent for pursuing such a strategy,

Finally, nothing was said here regarding the well-known importance of surface composition on the adsorption behavior of activated carbons. It was decided that the emphasis in this study should instead be on the extent of development of porosity and its nature; once formed, suitable porosity can have its surface character changed by well-established methods involving gaseous and liquid reagents. No amount of surface chemical modification can fundamentally change the suitability of a carbon for adsorption applications if the necessary extent and size distribution of the

porosity is not available. Hence, it seemed appropriate to retain focus on this latter aspect.

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